Lancaster Environment Centre

Lancaster University

Development of regionalized multimedia chemical fate models for China

Ying Zhu

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Abstract

To balance the economic development with environmental safety and human health, China has released chemicals management legislation for which chemical prioritization and risk assessment are key issues. To support these ambitions two versions of an environmental fate and behaviour model SESAMe (Sino Evaluative Simplebox-MAMI models), have been developed with different resolutions and structures in this thesis. SESAMe is applied to hypothetical chemicals to investigate the influence of environmental parameters on chemical persistence and long-range transport potential. The environmental distribution of benzo[a]pyrene (BaP) in the base year of 2007 and future scenario in 2030 in China has been predicted using SESAMe v3.0. The efficiency of different technical improvements on reducing emissions and environmental concentrations is discussed using the future scenario. Six organic chemicals, triclosan (TCS), triclocarban (TCC), climbazole, benzophenone-3 (BP-3), octocrylene (OC) and octyl methoxycinnamate (OMC), have also been modelled by SESAMe v3.3 to account for the chemical ionisation and the effect of environmental pH to chemical partitioning. The emission inventories of the six chemicals were estimated for 2012. TCS is used as an example chemical to explore the pH dependent environmental risk assessment for ionisable chemicals. Only limited freshwater areas in China were found to be in exceedance of TCS threshold levels. The influence of projected population, infrastructure, and environmental conditions on the use, emission and environmental distribution of the same six chemicals in 2030 was investigated. Infrastructure development, such as wastewater treatment plants (WWTPs) was shown to be the most important factor that will reduce the chemical emission and environmental concentrations into the future.

SESAMe models have been successfully applied to a chemical released to air and other types of chemicals released to water that are subject to potential ionisation. Model estimation is demonstrated to be good by comparison with the monitoring data collected from the literature. The application of current and future scenarios demonstrates SESAMe models are potentially

useful to support chemical management in China and to identify key gaps for chemical screening and risk assessment.

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Contents

List of papers

I. Ying Zhu, Oliver R. Price, Shu Tao, Kevin C. Jones, Andy J. Sweetman. A new multimedia contaminant fate model for China: How important are environmental parameters in influencing chemical persistence and long-range transport potential? *Environ Int*, 2014, 69: 18-27.

Ying Zhu developed the model, conducted the research and wrote the paper, with supervision from Andy J. Sweetman, Kevin C. Jones, Oliver R. Price and Shu Tao.

II. Ying Zhu, Shu Tao, Oliver R. Price, Huizhong Shen, Kevin C. Jones and Andrew J. Sweetman. Environmental distributions of benzo[a]pyrene in China: current and future emission reduction scenarios explored using a spatially explicit multimedia fate model. *Environmental Science & Technology*, 2015, 49 (23): 13868-13877.

Ying Zhu developed the model, conducted the research and wrote the paper with data and technical support from Huizhong Shen and Shu Tao, with supervision from Kevin C. Jones, Andrew J. Sweetman, Shu Tao and Oliver R. Price.

III. Ying Zhu, Oliver R. Price, John Kilgallon, Cecilie Rendal, Shu Tao, Kevin C. Jones and Andrew J. Sweetman. A multimedia fate model to support chemical management in China: a case study for selected trace organics. Submitted to *Environmental Science & Technology*.

Ying Zhu conducted the research and wrote the paper with supervision from Kevin C. Jones, Oliver R. Price, Andy J. Sweetman, and Shu Tao. Ying Zhu, Oliver R. Price and Andy J. Sweetman designed the idea. John Kilgallon provided data support on market size of consumer products and Cecilie Rendal provided the technical support on chemical space figure (Figure 1).

IV. Ying Zhu, Oliver R. Price, John Kilgallon, Yi Qi, Shu Tao, Kevin C. Jones and Andew J. Sweetman. Projected changes in environmental conditions, population, infrastructure and consumer spending on the use, emission and environmental distribution of selected organic chemicals in China. Draft included in thesis.

Ying Zhu conducted the research, projected the future scenarios and wrote the manuscript with supervision from Kevin C. Jones, Oliver R. Price, Andy J. Sweetman, and Shu Tao. John Kilgallon provided the data support on market size of consumer products. Yi Qi projected and provided the future population in 2030.

1. Chemical management regulations

1.1 The benefits and potential risks of chemicals

People's daily life and the development of human society rely on thousands of manufactured chemicals, such as ingredients in personal care products (PCPs) for ultraviolet light screening, antibacterial protection and insect repellence; pharmaceuticals for disease treatment and prevention (human use) or for husbandry (veterinary use); pesticides for crops protection and yield improvement, and flame retardants for prevention of the spread of fire and other industrial chemicals. There are already about 8,400,000 commercially available substances according to the CAS web site (CAS 2006). Global chemical production has now risen to over 400 million tonnes annually (Motaal 2009). The growth rate is predicted to double in about 22 years from the current year (2015) with a continuous growth of 3% per year due to the expansion of market demand (Wilson and Schwarzman 2009).

The current socioeconomic benefits of these chemicals are evident, e.g. improving quality of life and promoting technical development. However, on the other side, the potential risks of synthetic chemicals to human health or environmental safety had not been widely realized by the public until the publication of 'Silent Spring' in 1962, which raised concerns about the environmental persistence of pesticides and their adverse effects to humans and the environment. There are potential risks for many other chemical categories, e.g. including those chemicals stated earlier which as they can be released during synthesis, manufacture, use and during the waste cycle. Such chemicals can enter into and/or partition in single or multiple environmental compartments where they can potentially bioaccumulate and be toxic to humans or other organisms when concentrations are above particular thresholds. For example, benzo[a]pyrene，which is emitted by incomplete combustion of organic materials, can partition into multiple compartments and are known to be carcinogenic. Many pesticides are persistent and can become food chain contaminants as well as being transported to remote regions such as the Arctic (Rezg et al. 2010; Weber et al. 2010). Personal care product ingredients have also been reported to be toxic to biota above certain concentrations (Brausch and Rand 2011).

To prioritise the potential risks of chemicals and to aid chemical management, guidelines and legislation have been established internationally. The U.S. Environmental Protection Agency (USEPA), the OSPAR Convention for Protecting and Conserving the North-East Atlantic and its resources and the Stockholm Convention on Persistent Organic Pollutants (POPs) (OSPAR 1992; Stockholm 2011; USEPA 2012b) have established PBT (Persistent Bioaccumulative and Toxic substances) assessment schemes for chemical screening and management; however, such scheme only cover a relatively small group of hazardous chemicals. European chemical regulation on the Registration, Evaluation, Authorisation and Restriction of Chemicals (EU REACH) was enacted in 2007 (European Commission 2006); with a navigator tool developed by the European Chemicals Agency (ECHA) for supporting EU REACH has assessed 13931 registered substances (till 16 March 2016, http://echa.europa.eu/home). Meanwhile, the International Programme on Chemical Safety (IPCS, 1980) has been established jointly by WHO (World Health Organization), ILO (International Labour Organization) and UNEP (United Nations Environment Programme) in 1980 to strengthen the national capability and capacity for addressing chemical safety for human health and the environment. Such legislation and programmes demonstrate the high level importance of chemicals management internationally.

1.2 Chemical management regulations in China

As an important component of the world market, the Chinese chemical industry has been growing rapidly in the past 40 years (OECD 2001). Until now there are about 42,000 chemicals listed in the Inventory of Existing Chemical Substances Produced or Imported in China (IECSC) (MEP 2013). The market growth for chemicals China is predicted to account for about 60% of global growth in demand between 2011 to 2020 (Hong et al. 2013), which is determined not only by strong and stable manufacturing within China but also from imports. This continuously brings new chemicals into the Chinese market and potentially the environment. The Ministry of Environmental Protection (MEP) of China introduced the 'Provisions on the Environmental Administration of New Chemical Substances in China' in

2010 (MEP 2010), which is a framework similar to EU REACH for chemicals regulation. The 'new chemicals' identified in the regulation are those new to the market or imported chemicals which are not listed in the IECSC. Companies are required to prepare documents with information including chemical properties, toxicity, ecotoxicity, hazard and environmental risk for registration, which is similar to the EU REACH requirements. To regulate the methods used in the chemical risk assessment, the MEP drafted the 'Chemical Risk Assessment Guideline (proposal)' in 2011 (MEP 2011), which is applied to both chemicals already listed in IECSC and any new chemicals.

1.3 Problem definition and objectives

Risk characterization is a key step of risk management and environmental risks are normally expressed as a ratio of PEC/PNEC (PEC, predicted environmental concentration; PNEC, predicted no effect concentration) in many international regulatory frameworks (Van Leeuwen and Vermeire 2007). PNECs can be derived from chemical toxicity or ecotoxicity data from exposure tests. For the derivation of PECs, multimedia chemical fate models have been developed and applied in many countries in their regulatory frameworks. For example, EUSES (European Union System for the Evaluation of Substances) has embedded the Simplebox model (Vermeire et al. 1997); PBT Profiler (Persistent, Bioaccumulative and Toxic Chemical Profiler) has a Level III multimedia model for estimating the P, B and T to compare with EPA criteria (USEPA 2012b); a series of Level I to Level IV multimedia models have been used for the Canadian Environmental Protection Act (CEPA) (Webster et al. 2005); and OECD also has adopted a multimedia model as its chemical screening tool for chemical persistence and long-range transport potential (LRTP) (Wegmann et al. 2009). These models have been demonstrated to be important tools in the chemical risk assessment procedure for scientific research and policy making. Figure 1 shows the workflow of chemical risk assessment and the role of multimedia chemical fate models.

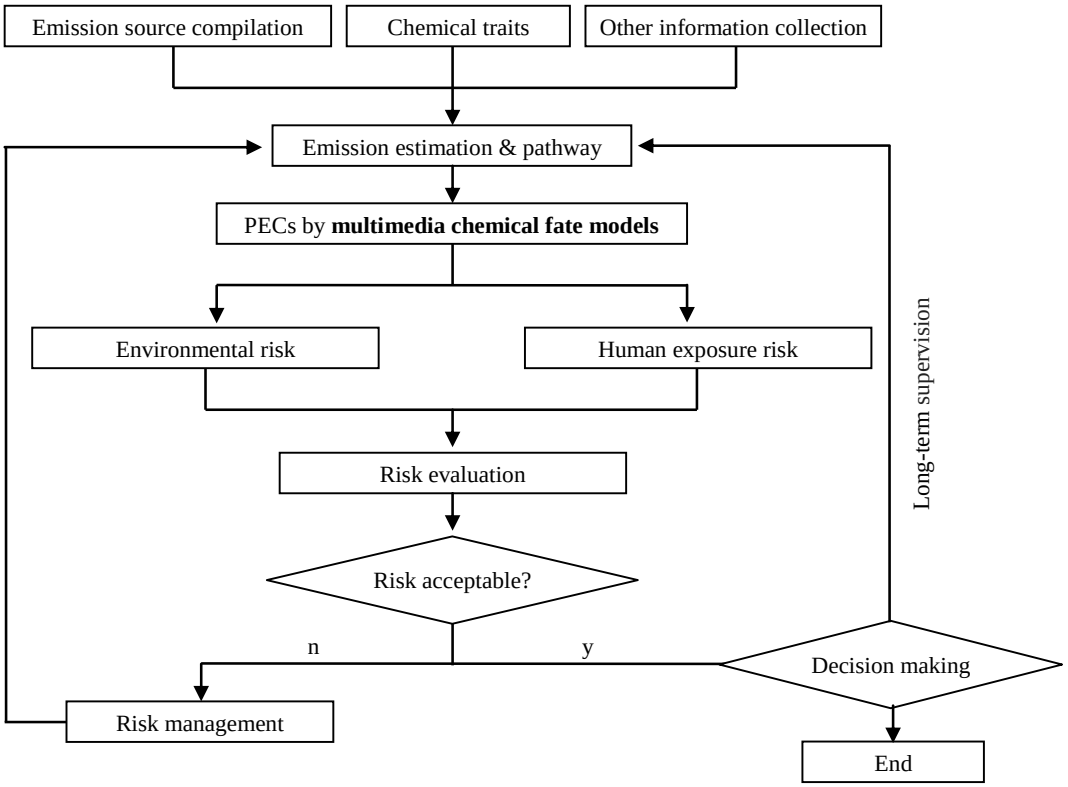

Figure 1 Work flow of chemical risk assessment and role of multimedia chemical fate models; PEC, predicted environmental concentrations

However, so far above models have only been developed for neutral chemicals. Ionisable chemicals have different environmental partitioning, transport or exposure pathways compared with neutral chemicals and subsequently have not been considered in these models. For risk assessment of chemicals in China, one of the gaps is the lack of a spatially explicit national scale multimedia chemical fate model for the derivation of PECs. The objectives of this PhD programme were therefore to

(1) Develop and parameterize a series of multimedia chemical fate models for China, which are capable for both neutral and ionisable chemicals - SESAMe models.

(2) Investigate the influence of diverse environmental conditions on overall persistence (P_{OV}) and LRTP of both neutral and ionisable chemicals in China, which has been discussed in **paper I**.

(3) Apply the models for a typical of chemical released to air (benzo[a]pyrene (BaP)) in **paper II** and another type of chemical (PCPs) mainly released to freshwater in **paper**

III and test/validate models by comparing model predictions and measurements collected from the literature to assess model performance.

(4) Examine model capability to assess partitioning and fate of ionisable chemicals in the environment and the sensitivity to environmental pH, thus exploring pH dependent environmental risk assessment as shown in **paper III**.

(5) Illustrate the potential role of the SESAMe models in research and as a support tool for future chemicals management and governance planning, by projecting future scenarios for China up to 2030 as shown in **paper II** and **paper IV**.

2. Multimedia chemical fate models

2.1 Evolution and types of multimedia chemical fate models

Mackay D. and Paterson S. pioneered multimedia environmental models in the late 1970s through to the beginning of 1980s. The models they developed were a group of models with four levels with different assumptions and levels of sophistication for the purpose of predicting the environmental behaviour and effects of chemicals (Mackay 1979; Mackay and Paterson 1981; Mackay and Paterson 1982). They adopted the concept of 'evaluative' model structures introduced by Baughman and Lassiter (Baughman and Lassiter 1978), which describe a fictitious but realistic environment, i.e. not for specifically real areas but reflecting probably chemical behaviours in the environment. These models are so-called box models which have linked environmental compartments typically including air, soil, water, sediment and biota and are assumed to be homogenous within each compartment. Complexity increases from Level I to Level IV models. Level I models show a closed system with equilibrium partitioning of chemicals between compartments without reactions. Level II models are open systems at equilibrium considering chemical degradation and advective inflow and outflow. Level III models are steady state with constant chemical input but non-equilibrium between compartments and include degradation and intermedia chemical transfer. Level IV models are dynamic with varied chemical emission rates with time (Mackay 2001). Due to the different

assumptions and definitions of the four levels of model, they can be used for different purposes or scenarios.

Building on Mackay's work especially for the Level III and Level IV models, different types of multimedia models with different structures and targeted chemicals have been further developed or parameterized over 30 years for assessing 'real' environments, e.g. a specific region, continent or hemisphere. The predictions by Level III models are usually accepted in chemical exposure assessment. The two types of models have been playing an important role in scientific study and chemical regulatory framework (MacLeod et al. 2010).

2.1.1 Fugacity, concentration and activity models

Multimedia chemical fate models mainly comprise three types according to the types of model output variables, i.e. fugacity, concentration or activity. The fugacity approach was proposed initially by Mackay (1979) in early multimedia environmental models, or so-called Mackay models, and demonstrated to be useful to describe the steady and dynamic behaviours of neutral organic chemicals (Mackay 1979). 'Fugacity' describes escaping tendency, which is identical to partial pressure in ideal gases and nearly proportional to concentration. It has been currently a major approach applied in many multimedia environmental models such as the EQC model (Mackay et al. 1996), the CalTOX model (McKone 1993), the CoZMo-POP2 model (Wania et al. 2006) and the BETR- North America model (MacLeod et al. 2001). The concentration approach, such as used in Simplebox model (den Hollander 2004), is a conventional approach when constructing multimedia mass balance matrix with rate constants.

The above two approaches are widely used in multimedia environmental models for neutral organic chemicals. Chemicals, such as ions, polymers or metals, which do not volatilise, cannot establish partial pressure or vapour phase concentrations. Fugacity or normal concentration approaches perform well for neutral chemicals but cannot describe ionisable chemicals; where an 'activity approach' is preferable. The concept of 'activity' was first defined by Lewis in 1907 (Lewis 1907) and adoption of activity in multimedia environmental

models can accurately describe thermodynamic equilibrium of charged or uncharged species in ideal and non-ideal solutions. The MAMI model (Multimedia Activity Model for Ionisable chemicals) was developed by Franco and Trapp (2010) using the activity approach; where they described the correlation of concentration and activity in their publication. As shown below, the MAMI model and activity approach are important references in this study to construct a multimedia environmental model capable for the assessment of ionisable organic chemicals in the Chinese environment.

2.1.2 Region-specific and multi-zone multimedia fate models

Region-specific (or regional scale) multimedia chemicla fate models are those parameterized for a specific region based on the evaluative model framework. The outputs of such models can be compared with reported chemical concentrations in the specific region directly. Examples of such models include ChemCan, ChemFrance, early version of Simplebox and Caltox. ChemCan is a Level III fugacity model parameterized for 24 independent ecological regions in Canada (Mackay 1991), and ChemFrance is a similar model with database of environmental parameters for 12 regions in France (Devillers et al. 1995). Early versions of Simplebox describe EU as a single zone (Van de Meent 1993). Caltox contains a geographical database for several regions of California, ten ecoregions of the US and 48 political regions of US states (McKone 1993).

Multi-zone/multi-region multimedia fate models are composed of interconnected regional scale multiemdia models by means of advective flows between air and water compartments. Examples of such models are the BETR series models, GloboPOP, SCHE and the last version of Simplebox, all of which have different structures. SCHE is a simplified global multimedia model developed by Scheringer (1996), which is a one-dimensional circular model composed of interconnected boxes. Each box contains only air, water and soil compartments. The other multi-zone models mentioned above are more accurate than SCHE with zonally distinct environmental parameters which aim to provide a more realistic and detailed description of a specific environment. The BETR North America (MacLeod et al. 2001) is the earliest BETR

model, which contains 24 ecological connected regions representing North American and each region consists of 7 environmental compartments. A European version of the BETR model was developed by Prevedouros et al (2004), Evn-BETR, which devided the whole Europe into 54 square regions. BETR-global is a similar model developed by MacLeod et al (2005) but covers the whole planet with 288 square regions of 15 °by 15 °each. GloboPOP by Wania and Mackay (1993) is a global model with a different structure to BETR-global. It has nine interconnected regions/zones indicating nine latitudinal bands, which are defined by global climate zones. Each region consists of four compartments (air, water, soil and sediment). The later versions of Simplebox, e.g. Simplebox 3.24a embeded in the EUTGD spreadsheet 1.24 (Huijbregts et al. 2008), have nested scales representing the global environment. The local scale is part of the regional scale, which is nested into a continental scale, with the continental scale nested into a moderate climate zone. Arctic and tropical zones are adjacent to the moderate zone. Each scale/zone is made up of air, water, sediment and three types of soils. Simplebox 3.24a was utilized to construct the multimedia fate model developed in this study, which will be described below and in **paper I** and **II**.

2.2 Multimedia environmental models developed and utilized for China

Researchers who aim to study chemical partitioning and fate in the Chinese environment have developed many regionally specific multimedia environmental models for China. Multimedia models have been well developed for Tianjin to study the fate of BaP (Wang et al. 2002), phenanthrene (Tao et al. 2003), γ-HCH (Cao et al. 2004; Tao et al. 2006) and p,p'-DDT (Li et al. 2006). Models have also been developed for other regions such as for Pearl River Delta (PRD) on PAHs (Lang et al. 2007), Lanzhou (Dong et al. 2009) and Liaoning (Liu et al. 2009) for HCHs, Bohai Bay for BaP (Liu et al. 2014) and some river basins such as the Yellow River (Ao et al. 2009) and Liao River (Liu et al. 2007). These are all fugacity models and applied on neutral chemicals. Multimedia fugacity models for national scale study have also been parameterized for China and utilized for ionisable chemicals, i.e. PPCPs (pharmaceutical

and personal care products), by Zhang et al. (Zhang et al. 2015a; Zhang et al. 2015b; Zhang et al. 2015c; Zhang et al. 2014).

3. Sino Evaluative Simplebox-MAMI (SESAMe) models

As the main aim of this thesis, the Sino Evaluative Simplebox-MAMI models (SESAMe) have been developed for China to provide information on environmental occurrence, partitioning and fate of chemicals, which should be readily accessible by decision makers.

3.1 SESAMe models development and description

SESAMe models are actually tight-coupled models of the Simplebox 3.24a and the MAMI III model parameterized for China (Figure 2). Technically there are three versions of the SESAMe model developed with different resolutions and structures, although only two versions (SESAMe and SESAMe v3.0/3.3) were finally adopted and applied to chemical studies as shown in **paper I-IV**. Although these models took the nested structure of the Simplebox 3.24a model (Figure 2A) and the activity approach of MAMI III (Figure 2B), they are neither multi-region models structurally the same as Simplebox 3.24a nor activity models. Based on all types of multimedia chemical fate models classified above, SESAMe models should be identified as Level III regional concentration models with a database of environmental parameters for 267 regions (SESAMe) and 5468 regions (SESAMe v3.0/3.3), respectively. Each region is a square grid cell composed of air, water sediment, three types of soils (urban, natural and agricultural) and two types of vegetation (natural and agricultural); SESAMe v3.0/3.3 considered seawater system in addition to SESAMe as to be stated below.

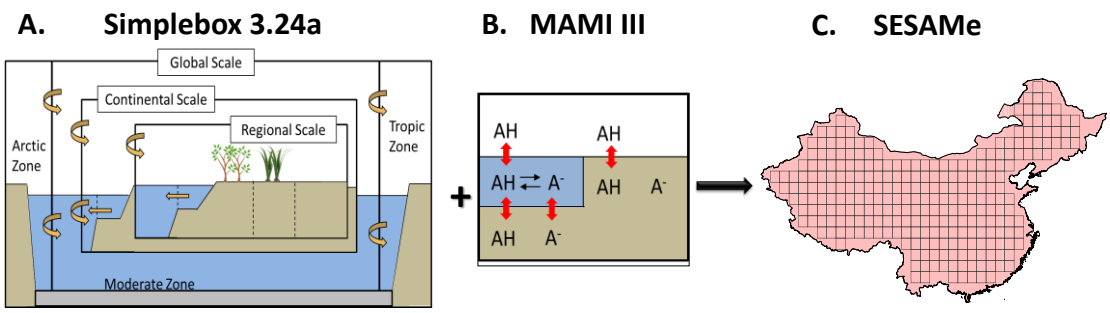

Figure 2 Diagram of feature of simplebox 3.24a, MIMA III and SESAMe

SESAMe models consist of two scales (regional and continental scale) of nested structure as shown in Figure 3. The details of the structure, formula and input parameters have been described in **paper I** and **paper II**, with a further update on environment pH in SESAMe v3.0, which is introduced in **paper III.** The version including the new environmental pH dataset has been named as SESAMe v3.3. The differences between the two versions are (1) a different regional scale size – 200 × 200 km^2 for SESAMe and 50×50 km^2 for SESAMe v3.0; (2) fixed continental scale defined as the whole continent of mainland China outside of the regional grid cell for SESAMe (Figure 3a), and a movable continental scale (150×150 km^2 square) composed of 8 adjacent grid cells surrounding the corresponding regional grid cell for SESAMe v3.0/3.3 (Figure 3b); (3) addition of seawater and sediment compartments in SESAMe v3.0/3.3, cells intersecting the boundary have also been included in SESAMe v3.0/3.3 but SESAMe only considers cells completely within the national boundary; (4) inclusion of agricultural soil irrigation by surface freshwater in SESAMe v3.0/3.3, which is a very important development as discussed in **paper III**; (5) more input environmental parameters were spatially resolved in SESAMe v3.0/3.3 instead of using a fixed default value, which is introduced in **paper II** and **paper III**. For the SESAMe model, the large fixed continental scale is an advantage for investigating the chemical P_{OV} and LRTP in China for chemical emitted to the regional scale, which is closer to the function of Simplebox in EUSES. For SESAMe v3.0/3.3, the main function of the continental scale is to realize the advective inflow and outflow in air and water compartments for regional scale.

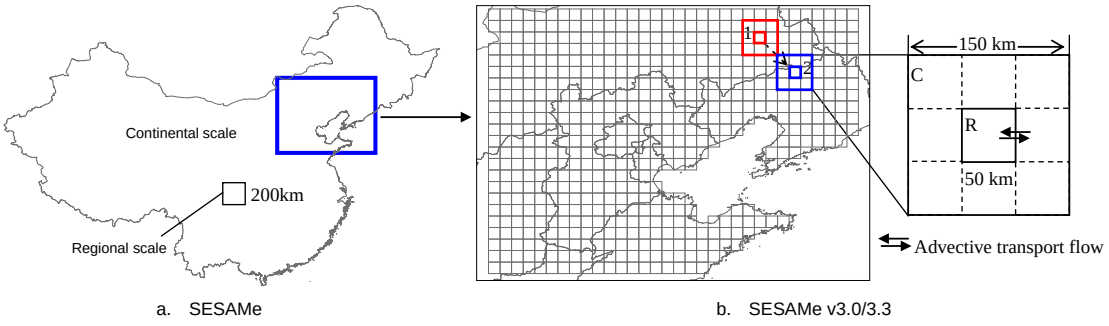

Figure 3 Structure and resolution of SESAMe and SESAMe v3.0/3.3; (b) R, regional scale; C, continental scale.

There is a transitory version, SESAMe v2.0, which has a 200×200 km^2 regional scale and a continental scale composed of its 8 adjacent regional grid cell (also 200×200 km^2 each). It has the same structure as SESAMe v3.0/3.3 but a coarser resolution. Therefore, it has not been adopted for predictions and publications as a finer resolution has been developed for improved prediction of extreme values.

The above provides an introduction to the model structures. The activity approach accounting for ionisable chemicals and different partitioning coefficients of neutral and ionic species in the environment has been described by Franco and Trapp (Franco and Trapp 2010). In order to understand the environmental processes important to ions in models are that (1) ions are non-volatile as shown in Figure 2B; (2) humidity has been considered for aqueous phases as 'aqueous water' associated with aerosol solids is important for partitioning and equilibrium with neutral molecules partitioning between gas phase and dry aerosol; (3) fractions of ionic molecules are calculated by the Henderson-Hasselbalch equation from environmental pH and chemical pKa; (4) the partitioning coefficients, including K_d (solid-water partitioning coefficient) and K_{OC} (soil organic carbon-water partitioning coefficient), are calculated separately for neutral and ionic species, and (5) logK_{OW} for ionisable chemicals (log$D$) is calculated using pKa and K_{OW} in neutral form.

The SESAMe models are different from MAMI III and are concentration models instead of the activity models. In MAMI III, activity is converted to concentration after the solution of the mass-balance matrix. SESAMe models complete the conversion before the solution of mass-balance matrix. SESAMe models have been extended to include vegetation compartments (natural and agricultural), which are not included in MAMI III. The formula for the partitioning of ions for vegetation compartments in the model is reported in **paper I**. The water compartment is assumed to be an ideal solution (i.e. pure water) in SESAMe models, which means that only a single chemical is assumed in the system so its ionisation will not be effected by species from other chemicals. In contrast, MAMI III accounts for non-ideal system behaviour and utilizes a factor used in thermodynamics to indicate deviations

from ideal behaviour in multiple chemicals solutions (activity coefficient) that is introduced in the model and calculated from default ionic strength assumed in MAMI III (Franco and Trapp 2010).

3.2 Model limitation and uncertainty

'*All models are wrong, but some are useful.*' – (Box and Draper 1987).

Mathematical models are established based on a series of assumptions which attempt to describe and simplify the complexity of the real world, but are believed to be useful as it is easier to obtain and study the response provided by a model than the response of the complex real world. Therefore, it is important for model developers and especially users to understand the principle limitations and uncertainties of SESAMe models to better understand the model and its potential application.

3.2.1 Limitations

Box models make assumptions about the homogenous nature of the environment, and the relatively large size of the boxes in SESAMe models can only provide an average chemical concentration of an area, and so cannot identify hotspots that are close to a point source. Level III models also determine concentrations and chemical transport or partitioning status only at steady state, as they cannot predict the dynamic change of chemical concentrations and behaviour over time. It is challenging to predict time-series concentrations and behaviours of chemicals using a dynamic (Level IV) multimedia model,as this depends on the availability of the temporal resolution of input environmental parameters for all environmental compartments and emissions. In such cases, some other more complex models, such as general circulation models (GCM) (e.g. Hysplit-4 and EMEP), can track chemical concentrations and behaviours with high spatial and temporal resolution in the atmosphere and oceans on a global scale. They include a meteorological database at various locations and altitudes over time in order to model chemical transport and fate in relation to geo-referenced

entities (e.g. land, sea, soil and vegetation) and entry mode of chemicals into the environment. However, such models are extremely data and processing power intensive.

The simplified approach used in multimedia chemical fate models such as the SESAMe models are unable to predict chemical behaviour with high spatial and temporal resolution. This is a general limitation currently for all multimedia chemical fate models not only for SESAMe. However, this is also an advantage of SESAMe models, as in many circumstances (e.g. large scale chemical screening level risk assessment, chemical prioritization or chemical environmental sink identification), more explicit predictions from models that parameterize the environment more realistically, such as Chemical Transport Models (CTM), are not required. It is also difficult, time-consuming with high data requirements to set up and use more complex models.

Another limitation of the SESAMe models is that due to the regional model structure, they can only study or identify the effects of environmental processes or emissions from surrounding regions to regional scale cell, but cannot directly capture the direction (mainly for the air and water compartment) of the effect and cannot track the spatial transport trajectories of chemicals from regional emission.

3.2.2 Uncertainty

The deviation between observed values and model results can derive from various types of uncertainties, which can be generally classified as informational uncertainties, model uncertainties and numerical errors (Loucks and van Beek 2005). These uncertainties can be introduced to the model with or without the knowledge of the user. It is easy to understand that sometimes imprecisions can result from a lack of knowledge, e.g. the difficulty of realizing complicated reactions between a particular species and environment or other species, or the inability to correctly evaluate the quality of acquired input parameters. Sometimes known uncertainties are introduced for simplification or other practical reasons.

Model uncertainties The model uncertainties that will be mainly discussed here concern input parameter values and model structure, and spatial and temporal variability of observed model input parameters which are related to model scale. For the model structure, a classic assumption for multimedia chemical fate model is the homogenous boxes/compartments. This assumes chemicals are well-mixed immediately after being released into compartments. In reality, complete mixing from point source emission to air is unlikely. This is especially true for point soil contamination, as soils are a relatively stable compartment in which chemicals do not easily migrate. Point sources can be universal such as the industrial emission to air and wastewater release from wastewater treatment plants (WWTPs). Another uncertainty caused by model structure is the nested structure especially for the first version of SESAMe model. Because the continental scale surrounds the regional scale and they are connected to each other by advective inflow and outflow in water and air but without differentiation of the flow direction especially for air compartment, the chemical contents in inflow to regional scale account for sum of chemical emissions to the continental scale. However, in reality, for example, the emission to air from a certain part of the surrounding area (continental scale) may not enter the regional scale due to the reverse wind direction. This probably causes regional overestimation of the effect of continental scale to regional scale but not at a national scale.

The input parameters to models include emissions, physico-chemical properties and environmental parameters. The uncertainty of emissions and physico-chemical properties will be discussed in later sections on emission inventories and target chemicals. For the environmental properties, the selection from unreliable data sources may result in uncertain values chosen as input. Especially when multiple data sources are available for one parameter, identification of the most appropriate or accurate one is important but difficult most of the time because they are rarely evaluated. Also, if input environmental parameters are taken from different data sources, uncertainty occurs especially when some of them show conflicting information so that important decisions have to be made on data selection. For the

SESAMe models, 19 spatially resolved environmental parameters are collated or projected for the 50×50 km^2 grid. Among them, the area fraction of freshwater was taken from a Chinese database (http://www.geodata.cn) and the river discharge flow was taken from a predictive model created by Mick J. Whelan as referred to in **paper I** and **II**. However, there are regions with area fractions of freshwater equal to 0 (i.e. no water) but river discharge flow greater than 0 in the same region. In such cases, 0 has been taken for all parameters relevant to volume of water compartment. This probably will cause regional error of model outputs but should not be important for large areas or at a national scale.

Observed data used as environmental input data for the model is normally spatially and temporally discontinuous and is on a different scale to the one that the model requires, which leads to variability. For the SESAMe models, the spatial resolution of observed environmental parameters is usually smaller than that of the model. For example, wind speed and freshwater pH are both from gauging stations sparsely located across China, so the interpolation method in ArcGIS has been used to obtain datasets with higher resolution to fit the SESAMe models. Such interpolation is mathematical prediction method without meteorological or hydrological understanding and therefore may lead to regional uncertainty. Another spatial variability occurs during the use of default environmental parameters. As indicated in **paper II**, there are approximately 47 fixed default environmental parameters in SESAMe v3.0. Many of them should have significantly spatial variation in the real world but cannot be reflected in the model owing to the lack of available spatially resolved data, e.g. organic carbon content and volume fraction of suspended particles in water, organic carbon contents in aerosol, and soil properties such as volume ratio of air, pore water and solids. It is important to obtain spatially resolved data for soil and air properties across China.

For the temporal variability, as SESAMe models are not dynamic, temporal information has been waived by averaging environmental parameters over a time-series to obtain mean values, e.g. long-term average precipitation, wind speed and river discharge flow. Precipitation and river discharge flow may be typical parameters which have such variability. In reality,

precipitation is not continuous and rivers have alternate dry and wet seasons. The continuous precipitation assumption in the model probably results in underestimation of air chemical concentration for some regions. The uncertainty caused by averaged river discharge flow could be more complex and difficult to quantity. Emission variation over time will also impact on model uncertainty.

Informational uncertainties and numerical errors Informational uncertainties include imprecisions in boundary and initial conditions which will impact model output whereas monitoring data will exhibit such variability. For SESAMe models, initial concentrations in environmental compartments are set at zero, in contrast, for many regions chemical residues will have existed before the time when emissions have been assumed to start. However, it is unrealistic to acquire spatially resolved chemical residue data China before this initial time. The boundary conditions are difficult problem for all environmental models, because the model spatial resolution has a physical size. Therefore the model cannot perfectly capture the whole area within the boundary but must exclude areas outside at the same time, unless the model resolution is infinitely high, which is impossible. This will cause the uncertainty in calculation process for boundary areas. The variability of monitoring data can also vary both spatially and temporally. This will be discussed in the model evaluation section. Numerical errors indicate mainly the errors in solution algorithm in models. Because the formulas in SESAMe models are almost directly taken from other two published models, numerical errors will not be discussed in this study.

3.3 SESAMe models application

Multimedia models have been identified as prominent tools for providing "scientific evidence" for assessing chemical persistence and LRTP by both scientific and policy communities (OECD 2004). The two indicators, P_{OV} and LRTP, reveal whether chemicals can potentially lead to continuous exposure in the future or be present in remote areas, and therefore they are widely used for the chemical screening and assessment. They derive from both chemical and environmental properties and the effect of chemical properties on Pov and LRTP has been

discussed by Fenner et al. (Fenner et al. 2005). The first SESAMe model (with a 200×200 km^2 grid) was applied on a series of hypothetical chemicals to investigate the effect of environmental properties accounting for the range and variability of chemical properties, as shown in **paper I**. Sobol sensitivity analysis was adopted to study such combined influence of input variables to model output with consideration of all chemicals. Example chemicals were selected as a case study for spatial variation of P_{OV} and LRTP in China using hypothetical emissions.

Using a finer resolution, SESAMe v3.0 was applied to predict the spatial distribution of BaP in the Chinese environment and the partitioning in environmental media to identify possible sinks for the chemical. Model validation was employed by comparing model predictions and measured data collected from approximately 130 peer-reviewed papers. BaP emission inventories for the year 2007 (Shen et al. 2013) was acquired for the predictions. Two future emission reduction scenarios were assumed and discussed to explore and compare the efficiency of different methods on reducing BaP concentrations in Chinese environment. The BaP concentrations in current and future scenarios were compared with the environmental quality guideline values. This work is detailed in **paper II**.

Paper III proposed SESAMe v3.3 as a potential support tool for chemical management in China, which can provide quantitative risk assessment by linking the chemical emissions and toxicity data. The model was therefore tested on selected organic chemicals, i.e. three antibacterial agents and three UV filters (shown below), to show its capabilities and advantages on ionisable chemicals accounting for the range and variability of environment pH. These chemicals were assumed to be only released to the freshwater compartment with emission inventories developed for the reference year 2012. Model validation was undertaken by comparing the predictions and measured data collected for major river basins in China from the literature. Environmental partitioning of chemicals in different media was calculated at steady state. A pH dependent environmental risk assessment method was suggested for

ionisable chemicals in this paper. Potential application of the model on water quality management and new chemical registration was also discussed.

Paper IV investigated the influence of projected environmental conditions, infrastructure development, population and consumer spending on chemical usage, emission and environmental distribution in China for the year 2030. The results were compared with those predicted for 2012 and discussed in **paper III**. Construction of infrastructure (mainly WWTPs) was identified as the most influential variable for reducing emission and ultimately environmental concentrations in China, which is also a factor more easily controlled compared to natural factors such as future river discharge flow. Such investigations are useful for providing reference information for research needs, government decision-making and business sustainability. Therefore, it is worth applying the model to future projections for other chemicals allowing discussion of different scenarios under a range of assumptions.

4. Studied chemicals

4.1 Studied chemicals and properties

Hypothetical chemicals were mainly used in **paper I** to discuss the effect of chemical properties on P_{OV} and LRTP. In order to cover a wide range of chemical properties, approximately 130 organic chemicals with values for most physico-chemical parameters were taken directly from the chemical database included in Simplebox 3.24a (Huijbregts et al. 2008) model. The values of parameters including degradation rates and enthalpy of vaporization were supplemented or updated by referring to a handbook of physicochemical properties (Mackay 2005). The chemicals covered 17 categories within the handbook, such as aliphatic and cyclic hydrocarbons, mononuclear aromatic hydrocarbon, PAHs and related aromatic hydrocarbons, halogenated aliphatic hydrocarbons, ethers, alcohols, insecticides, herbicides, fungicides and esters. Although several real example chemicals were chosen to indicate the spatial difference of P_{OV} and LRTP across China, chemical specific discussion was not employed using real emission scenarios.

Specific chemical studies using real environmental and emission scenario data were undertaken in **paper II-IV**, which targeted BaP (**paper II**) and other selected organic chemicals released to water (**paper III-IV**), i.e. six PCPs, respectively. The reasons for selecting these chemicals were:

1. Inclusion of two representative categories of chemicals, 'traditional' pollutants (BaP) and new chemicals of potentially emerging concern (PCPs);
2. Environmental persistence;
3. Concerns over chemical risk to the environment and human health;
4. Availability of well documented emission inventories or data for developing emissions for China;
5. Availability of relatively sufficient monitoring data across China for model validation;
6. Existence of data for toxicity, risk/unit risk or guideline values for chemical risk assessment.

Benzo[a]pyrene

There has been wide interest in emission sources, environmental concentrations and fate and potential carcinogenicity of PAHs. They are by-products of inefficient combustion of organic materials, so they exist ubiquitously in multiple media in the environment due to both natural and anthropogenic sources. Generally, emissions of PAHs have been declining since 1970s for developed countries and late 1990s for developing countries (Shen et al. 2013). However, the total emission for developing countries in 2007 was still approximately 4 times that from developed countries during their peak emission time (1970s), with China contributing 20% of the global emission in 2007 with a population of over 1.3 billion (Shen et al. 2013). Human exposure to PAHs can potentially occur through multiple pathways, e.g. inhalation of air or smoking, drinking water, food or soil contact and digestion. Without regard to smoking, the probable contribution of different exposure pathways to PAHs intake could be significantly different, such as food 96.2%, air 1.6%, water 0.2% and soil 0.4% (WHO 2000). However this could vary amongst individuals depending on the behaviour of a specific person, such as

occupation, cooking mode and dietary, location of residence. Also, different exposure routes may target different cancers, so it is important to develop knowledge on exposure concentrations in different media and corresponding risks rather than only focus on one compartment and exposure route which is main intake pathway (for example via food intake).

BaP was studied in **paper II** as it is the most well studied of the PAHs and usually used as an indicator to present carcinogenic PAHs. The detailed emission sources of BaP will be introduced in below in the section on emission inventory. **Paper II** contains a list of the values of chemical parameters used in model calculation.

Personal care product ingredients

In **paper III** and **IV**, six PCPs, i.e. triclosan (TCS), triclocarban (TCC), climbazole, benzophenone-3 (BP-3), octocrylene (OC) and octyl methoxycinnamate (OMC), were selected as example organic chemicals to investigate a group of substances mainly released to water. These chemicals, in contrast to BaP, are emerging environmental contaminants, of which limited information is known on their physico-chemical properties, possible emission sources, environmental occurrence, toxicity and risk to environment and human health. These are barriers/gaps for chemical management but also are driving force for innovation in environmental research with regard to their potential threats, e.g. the development of new analytical methods and improvement of models. Franco et al. (2010) concluded in their study that possibly about 49% of chemicals are ionisable based on a random sample of 1510 chemicals out of about 117,000 chemicals pre-registered at ECHA (Franco et al. 2010). As shown in **paper III**, the six chemicals cover acids and neutral chemicals with different pKa and Kow values. Physico-chemical properties used in this study are presented in **paper III**. The projection of environmental occurrence in the year 2030 for the same chemicals is presented in **paper IV**.

4.2 Uncertainty due to selection of physico-chemical parameters and toxicity data

The uncertainty owing to model definition and environmental parameters has been discussed above. Another source of uncertainty can derive from the selection of input chemical parameters. In the SESAMe models, chemical properties mainly include pK_a/pK_b, vapour pressure and water solubility (measure at 25˚C), Kow and degradation rates in air, water, sediment and soil. These parameters are key factors for determining chemical behaviour in environment such as chemical persistence, LRTP, partitioning between environmental media and advective transport. Priority should be given to available measured values as selection for input chemical parameters rather than model predictions. Chemical property estimation models/programmes usually predict parameters based on a single input of chemical structure without considering the feasibility of the training dataset to an individual chemical (Snyder 2009). For measured values, it is common for several varied values being reported in different studies for one specific chemical parameter of a substance (e.g. Table 1). If measurement data for chemical properties are not available, models/methods have to be selected carefully to generate the necessary data. The same issue exists for selection of toxicity data for quantitative risk assessment as application of the model output.

Table 1 Physico-chemical parameters

Chemical	Vapour pressure	Water solubility	logKow	pKa
BP-3	**1.1×10^{-3} Pa**[1] (i)	68.56 mg/L[3]	3.52[3]	9.57[5]
	7×10^{-4} Pa[2]	**6 mg/L**[1] (i)	3.79[4]	**9.54**[6]
			3.6[1] (ii)	8[4]
			4[2]	7.56[2]
Climbazole	**9.6×10^{-4} Pa**[1] (i)	8.281 mg/L[8]	3.5[7]	5.66[7]
		58 mg/L[1] (i)	3.76[3]	**7.5**[8]
			3.83[1] (ii)	
TCC	**4.6×10^{-11} Pa**[9]	0.045 mg/L[10]	3.5[10]	**12.7**[12]
		0.0237 mg/L[11]	**5.8** or 6[1] (ii)	
		0.6479 mg/L[3]	4.9[3]	
TCS	**6.93×10^{-4} Pa**[13]	4.621 mg/L[3]	**4.8**[1]	**7.9**[12]
	7×10^{-4} Pa[1] (i)	**8.8 mg/L**[1,a]		

Notes: 1. ECHA experimental result (ECHA);

2. Predicted values by SciFinder Scholar Database (Kim and Choi 2014);

3. Predicted values by EPI Suite (USEPA 2012a);

4. Predicted values by ALOGPS 2.1 (Wick et al. 2010);

5. Measured by Yang et al. (Yang and Ying 2013);

6. Measured by Castro et al. (Castro et al. 2003);

7. Unclear method (Casado et al. 2015);

8. Predicted values by ALOGPS 2.1 or EPI Suite (Chen et al. 2013);

9. Measured value in US EPA report (USEPA 2009);

10. Measured by Snyder et al. (Snyder et al. 2010);

11. Predicted values in ECHA database (ECHA);

12. Estimated by Loftsson et al. (Loftsson et al. 2005);

13. Unclear method (McMahon et al. 2008);

a. extrapolated by ECHA experimental data (3.6 mg/L at 10 ℃; 6.5 mg/L at 20 ℃; 10.8 mg/L at 30 ℃);
i, reliable without restriction; ii, reliable with restriction (ECHA).

For many emerging environmental contaminants chemical property estimation tools are needed to support the research on environmental exposure and risk assessment as few data are available. Such models/programmes include EPI Suite (USEPA 2012a), LFERs (Linear Free-energy relationships), ALOGPS 2.1 (Tetko and Tanchuk 2002) and ACD/Labs (http://www.acdlabs.com/). Reviews of chemical properties for the six PCPs in this study have been carried out to ensure the selected data is justifiable. Table 1 contains the values related to chemical partitioning for the four acids. Predictions are avoided, especially those provided by EPI Suite, as EPI Suite is likely to erroneously estimate the chemical parameters related to partitioning for ionisable chemicals, such as water solubility and Kow (Snyder et al. 2010). Therefore, the measured values (highlighted as bold in Table 1) with higher reliability (marked with 'i' in bracket) are adopted. Few data has been found on degradation rates for the selected chemicals, so predictions by EPI Suite were adopted and are shown in **paper III**. However, it is clear from Table 1 that values from different sources vary greatly such as pKa of BP-3 ranging from 7.56 to 9.57. If compared to the normal environmental pH of freshwater in China which is approximately 6.8-8.9, such discrepancy would result in significant uncertainty when calculating chemical partitioning and transport between freshwater and sediment. A similar bias can occur in reported data for risk assessment thresholds. For example, the reported PNEC of TCS in water ranges from 26.2 to 1550 ng/L (indicated in **paper III**).

5. Emissions Inventory

Emissions inventories are probably the most important model input that determine the predicted chemical concentration in the environment It is also a major barrier for modelling research owing to lack of methods or availability of data for accurate emission estimation. In this thesis, emission inventories were developed by the author for the three antibacterial agents and three UV filters for year 2012, which is used in **paper III**. The emission inventory of BaP used in **paper II** was developed by Shen et al. (Shen et al. 2013). The uncertainty derived from development of the emission inventories will be discussed below, so the methods will be introduced briefly for both BaP and the six PCPs.

5.1 Emission of BaP and uncertainty

Development of emission inventory The emission inventory for BaP for the base year 2007 utilized in **paper II** was developed by Shen et al. (2013). The atmospheric emission was calculated using fuel consumption and corresponding emission factors (EFs) of BaP. A global fuel consumption database (PKU-FUEL-2007) was created with 69 fuel consumption activities and disaggregated to a resolution of 0.1 °×0.1 °. The fuel consumption activities can be found in the Supplementary Information of the publication by Shen et al. (Shen et al. 2013). The 69 activities were divided into six categories by fuel types, i.e. coal, petroleum, natural gas, biomass, solid wastes and an industrial process category; or six sectors by use, i.e. industry, energy production, transportation, residential and commercial source, agriculture and deforestation and wildfire.

Shen et al. (2013) compiled 5822 measured EFs reported for PAHs. They were used to estimate the EFs for sources for different sectors. The methods were (1) regression modelling using per capita GDP (purchasing power parity) for transportation, (2) technology splitting to two or three technical divisions for each source for industrial and anthropogenic biomass burning sources based on different emission mitigation measures, and (3) fixed default values for all other sources regardless of temporal and national change. For EFs estimation in (2), the

ratio of different technologies applied over time annually can be calculated as described in **paper II**, which was also referred to the study by Shen et al. (2013).

From Shen et al.'s study, there were about 1032 tonnes BaP emitted in 2007 in mainland China (exclusive of Taiwan and Hainan). Nationally, the composition of BaP sources in China is 43% indoor biomass burning (firewood and crop residue), 21% coke production, 12% primary Al production, 13% domestic coal burning, 2% motor vehicle and 1.2% open fire agriculture waste burning. This is referred to in the study on future emission scenarios in **paper II**.

In **paper II**, two future hypothetical emission reduction scenarios were developed based on the importance/contribution of different sources used in the current scenario (2007). The assumptions for the future emission scenarios were that (1) coal consumption in 2030 will be the same as that in 2007 in the energy production and industry sectors but technology will be improved for Scenario 1 (Sc1); and (2) indoor biomass burning for cooking and indoor space heating will be reduced by 50% in some regions by 2030 and meanwhile technology will be improved, and the open burning of biomass will be prohibited by 2030 for scenario 2 (Sc2). Considering such efficiencies across a large country, this technological improvement was only employed in areas with a contribution of corresponding source in each scenario > 50% to all sources or with the predicted air concentration in current scenario > 1ng/m^3. The detailed assumptions for future emission scenario for nominal year 2030 can be found in **paper II**.

Uncertainty The emission inventory developed by Shen et al. is the most comprehensive and accurate database that is currently available. However, uncertainty still exists and varies for different countries as a result of data availability, for example, there is a lack of data acks for certain large countries such as Indonesia and Argentina (Shen et al. 2013). For China the resolution of fuel consumption data collected for emission estimation is better than the other countries included in their study (Wang et al. 2013). This can reduce the uncertainty of the estimation for China compared to other countries. However the EFs are applied at a national

level without spatial variation across the country. For example, the per capita GDP used for regression modelling is applied at a national scale and the ratio of different technologies based on emission mitigation measures applied is identical across the country. Therefore, regional uncertainties are likely to exist.

5.2 Emission of six PCPs and uncertainty

Development of emission inventory. Methods of emission estimation were the same for the six PCPs. The detailed methods have been described in **paper III**. The following data were collected for emission estimation for the reference year 2012, (1) the volume of products containing the six chemicals sold in Chinese market at the national level; (2) fraction of variants (productions that have the same or similar function but different brands) which contain the target chemicals at the national level; (3) fraction of wastewater connected to WWTPs respectively for rural and urban areas at the provincial level; (4) removal ratios of chemicals in WWTPs. The first two above were for estimating the chemical usage. The allocation method across China has been introduced in **paper III**.

The future emission scenario for the year 2030 was developed in **paper IV** for the same six chemicals. The fractions of variants containing the target chemicals and chemical removal ratios in WWTPs in 2030 were assumed to be the same as the reference year 2012. Future sales data for the year 2030 were predicted using regression modelling of history sales data and per capita GDP and the projection of per capita GDP by OECD. Future WWTPs construction was estimated based on the increasing rate over the past ten years. Future domestic water use was estimated at provincial level for predicting the sewage connectivity combining the future WWTP construction.

Uncertainty Possible uncertainty may derive from following factors: (1) in **paper III** the assumption that all products sold in 2012 would be used and released within the same year could possibly lead to overestimation, however, the products sold in last year (2011) could still remain in use in 2012 but would not be included in our estimations; (2) the fraction of

product variants containing target chemicals is based on average data estimated from historical data from 1990 untill 2012 in the Mintel database (http://www.mintel.com). As the annual data in the Mintel database only includes new products launched in the market every year, historical data from 1990 to 2012 should contain all the variants launched to market during these years but would not consider phased-out variants; (3) chemical removal ratios in WWTPs are assumed to be identical across the country which may lead to uncertainty as different WWTPs with different technologies behave differently; (4) the future predictions for the year 2030 in **paper IV** may contain some uncertainties as the estimation and assumptions are included in only one scenario as discussed in **paper IV.** Therefore different scenarios could be investigated in future studies for a more comprehensive analysis.

6. Model evaluation

6.1 Monitoring data collection

In **paper II** and **III**, monitoring data was collected for validating the model on BaP and the six PCPs. In **paper II**, about 130 peer-reviewed literatures were reviewed for collecting the measured data of BaP in air, water, sediment, soils and vegetation. Coordinates of sampling sites were mostly provided in these literatures. These data reflects the current concentration at specific point sites, while model predictions indicate the temporal and spatial average concentration in each grid cell. Therefore, more sampling sites falling in the same grid cell which could cover different time in a year would possibly ensure better match of predictions and measurements. In **paper III**, peer-reviewed literatures were collected for model validation on the six PCPs. In contrast to BaP, papers published on environmental occurrence of the six chemicals are far less than those for BaP, and also the coordinates of sampling sites were normally not provided. Therefore, the comparison of model predictions and measurements was based on river basin level, which could possibly lead to greater uncertainty. However, similar as the validation for BaP, more sampling sites relative to the area of the river basin could possible ensure a better match of predictions and measurements.

6.2 Sensitivity analysis and Monte Carlo simulation

Two sensitivity analysis methods are used in the study in **paper I-III**. In **paper I**, Sobol sensitivity analysis is used to study the effect of individual input parameters and their combined effects on model output. This method considers the range and variation of each input parameter and allows all input parameters to change together at the same time. In **paper II-III**, the SCV (variability-based sensitivity coefficient) method is used to implement the sensitivity analysis. This method also considers the range of the input parameters. If comparing the two sensitivity analysis methods, the Sobol sensitivity analysis differentiates the contribution from individual parameters and the combined effects of any two parameters, however, it can take a long time to complete; SCV costs less time but cannot differentiate the contribution to the model output is from a single parameter or combined effects. In **paper II-III,** Monte Carlo simulation has been implemented to estimate the uncertainty.

7. Discussions and conclusions

Paper I-IV aims to introduce multimedia chemical fate models developed and parameterized for China, the SESAMe models, and depicts the application of models on different types of chemicals for the purpose of chemical risk assessment and management. **Paper I** investigates the importance of input variables especially environmental variables of the SESAMe model to chemical P_{OV} and LRTP. To study spatial variation, P_{OV} and LRTP of several real chemicals were investigated with a fixed hypothetical emission, i.e. dibenzofuran (DF), BaP, acenaphthene (ACE) and TCS. **Paper II** validates SESAMe v3.0 using BaP and explores the spatial variation of concentration in multiple media across China, the partitioning between media and future concentration trends for BaP under two emission reduction scenarios to identify efficient emission mitigation strategies. **Paper III** extends the research and model application to other organic chemicals and reveals the advantage of SESAMe v3.3 for ionisable chemicals and a pH dependent environmental risk assessment. Chemical partitioning between environmental media are explored for these chemicals only released to freshwater. **Paper IV** projects the future scenario for 2030 to explore the influence of the

changing factors such as chemical use, emission and environmental concentration across China.

Paper I It was found in **paper I** that physicochemical parameters are generally more important than environmental parameters in determining P_{OV} and LRTP, although certain environmental parameters were also influential, such as precipitation, wind speed, temperature and soil organic carbon content (soil OC). Among those more influential environmental parameters, P_{OV} is more sensitive to precipitation than the other environmental parameters; LRTP is more sensitive to wind speed than the other environmental parameters. Soil OC has slight effect on P_{OV} and LRTP and higher soil OC always increases P_{OV} and decreases LRTP. For example, chemical case studies on spatial variation showed that DF released to air, water, urban and agricultural soils has higher P_{OV} in northwest of Xinjiang, part of Gansu, northeast of Inner Mongolia, Heilongjiang and Jilin owing to the higher soil OC in these areas. Both released to the atmosphere, BaP has higher LRTP in south Xinjiang and west Inner Mongolia due to lower precipitation, meanwhile ACE has a higher LRTP in Tibet and west Inner Mongolia due to the high wind speed in these regions. For chemicals released to water such as TCS, discharge flow has strong influence on LRTP, so TCS has higher LRPT in Yellow River and Yangtze River catchments.

Paper II Model validation for SESAMe v3.0 shows that the model performs well in predicting multimedia concentration and distribution. Areas of predicted concentration with exceedance of guideline values are mainly in the North China Plain (NCP), Mid Inner Mongolia, parts of three northeast provinces, Xi'an, Shanghai, south of Jiangsu province, East Sichuan Basin, middle of Guizhou and Guangzhou. The spatial pattern of predicted concentration and emission is similar, however, environmental conditions can produce contrasting regional air and soil concentrations. Emission decreases from 1032 tonnes to approximately 900 tonnes in Sc1 and to about 600 tonnes in Sc2 per year. **Paper II** concludes that Sc2 is more efficient than Sc1 in reducing areas with exceedance of guideline values. For example, using 2.5 and 1 ng/m^3 as air quality guideline values, areas with exceedance are

reduced by about 19 and 6% in Sc1 and about 51 and 40% in Sc2. However, the efficiency in Sc2 is not simply attributed to indoor biomass burning being the major source. It is important to reduce the emission not only in regional area but also in surrounding regions as shown in Figure S10 in **paper II**.

Paper III This paper demonstrates good performance of SESAMe v3.3 for ionisable chemicals. The areas with higher predicted concentrations are in NCP, Liao River basin, Jiangsu and coastal areas in Zhejiang, Fujian and Guangdong provinces. The pattern of spatial distribution of emission and predicted concentration in water and sediment is similar for all six chemicals, however, regional contrasts exists mainly due to discharge dilution. The fate and partitioning of acids such as TCS and climbazole are sensitive to environmental pH, as their pKa is within the range of the environmental pH. Soils are found to be important storage compartments, or even primary, for these chemicals are emitted to soil as a result of agricultural irrigation. The pH dependent risk assessment suggests that approximately 0.03% of freshwater areas (about 55 km^2) probably exceed the conservative environmental no-effect threshold for TCS.

Paper IV The future scenario projecting chemical emissions to 2030 indicates the construction of infrastructure will be the most important factor that reduces the emission and environmental concentrations of the six chemicals. Future river dilution with consideration of global warming also contributes to the reduction of predicted environmental concentrations.

8. Future perspectives

Based on above discussions, SESAMe models have been shown to be potentially capable to support chemicals management in China. They can be used for a broad range of chemicals, such as pharmaceuticals, as long as the estimation of emission is achievable. Accuracy of some environmental parameters or processes can be improved, such as the agricultural soil irrigation process in the model, so that the regional uncertainty of prediction could be reduced.

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A new multimedia contaminant fate model for China: How important are environmental parameters in influencing chemical persistence and long-range transport potential?

Ying Zhu [a], Oliver R. Price [b], Shu Tao [c], Kevin C. Jones [a], Andy J. Sweetman [a,*]

[a] Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, United Kingdom
[b] Safety and Environmental Assurance Centre, Unilever, Sharnbrook MK44 1LQ, United Kingdom
[c] College of Urban and Environmental Sciences, Peking University, Beijing 100871, China

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ABSTRACT

We present a new multimedia chemical fate model (SESAMe) which was developed to assess chemical fate and behaviour across China. We apply the model to quantify the influence of environmental parameters on chemical overall persistence (P_{OV}) and long-range transport potential (LRTP) in China, which has extreme diversity in environmental conditions. Sobol sensitivity analysis was used to identify the relative importance of input parameters. Physicochemical properties were identified as more influential than environmental parameters on model output. Interactive effects of environmental parameters on P_{OV} and LRTP occur mainly in combination with chemical properties. Hypothetical chemicals and emission data were used to model P_{OV} and LRTP for neutral and acidic chemicals with different K_{OW}/D_{OW}, vapour pressure and pK_a under different precipitation, wind speed, temperature and soil organic carbon contents (f_{OC}). Generally for P_{OV}, precipitation was more influential than the other environmental parameters, whilst temperature and wind speed did not contribute significantly to P_{OV} variation; for LRTP, wind speed was more influential than the other environmental parameters, whilst the effects of other environmental parameters relied on specific chemical properties. f_{OC} had a slight effect on P_{OV} and LRTP, and higher f_{OC} always increased P_{OV} and decreased LRTP. Example case studies were performed on real test chemicals using SESAMe to explore the spatial variability of model output and how environmental properties affect P_{OV} and LRTP. Dibenzofuran released to multiple media had higher P_{OV} in northwest of Xinjiang, part of Gansu, northeast of Inner Mongolia, Heilongjiang and Jilin. Benzo[a]pyrene released to the air had higher LRTP in south Xinjiang and west Inner Mongolia, whilst acenaphthene had higher LRTP in Tibet and west Inner Mongolia. TCS released into water had higher LRTP in Yellow River and Yangtze River catchments. The initial case studies demonstrated that SESAMe performed well on comparing P_{OV} and LRTP of chemicals in different regions across China in order to potentially identify the most sensitive regions. This model should not only be used to estimate P_{OV} and LRTP for screening and risk assessments of chemicals, but could potentially be used to help design chemical monitoring programmes across China in the future.

1. Introduction

With the rapid development of the Chinese economy, the production, manufacture and consumption of chemicals has increased sharply over recent years. This has inevitably resulted in the detection of residues of pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCBs), polybrominated diphenyl ethers (PBDEs) and emerging chemicals like pharmaceuticals and personal and household care product ingredients (PPCPs) in the environment including water (Bai et al., 2008; Zhao et al., 2010), air (Wang et al., 2012), soil (Wang et al., 2009, 2010), biota (Yuan et al., 2014) and food (Wang et al., 2013). The fate and behaviour of these chemicals in the diverse Chinese environment has increasingly attracted scientific and political interest, with particular concerns arising from human exposure to these chemicals via the environment. The Ministry of Environmental Protection (MEP) of China published the amended version of Provisions on Environmental Administration of New Chemical Substance in 2010 (MEP, 2010), which is similar to the EU REACH guideline (European Commission, 2006), and provides a risk based approach to chemical management. It is well recognized that the potential for harmful effects

* Corresponding author.
E-mail addresses: y.zhu6@lancaster.ac.uk (Y. Zhu), Oliver.Price@unilever.com (O.R. Price), taos@pku.edu.cn (S. Tao), k.c.jones@lancaster.ac.uk (K.C. Jones), a.sweetman@lancaster.ac.uk (A.J. Sweetman).

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of chemicals is not limited to areas of close proximity to their use but also to remote and vulnerable ecosystems (Matthies et al., 2009). Overall persistence (P_{OV}) and long-range transport potential (LRTP) are two metrics that are widely used to determine the chemical fate and potential environmental concern. They are determined by both chemical and environmental properties and are reliant on model predictions in a particular geographical region (OECD, 2004). Multimedia models have been developed as valuable tools to calculate P_{OV} and LRTP of chemicals (Fenner et al., 2004; Klasmeier et al., 2006; OECD, 2004). Such models can be used to investigate P_{OV} and LRTP characteristics for chemicals including those that are not yet introduced into an environment and to explore how the spatial variability in environmental conditions may impact. In general, it has been concluded that chemical properties largely determine the ranking of chemicals according to P_{OV} and LRTP. The effect of chemicals properties has been carefully discussed using hypothetical chemicals by Fenner et al. (Fenner et al., 2005). Though, environmental factors, especially climate, have been shown to influence chemical behaviour (Wania and Mackay, 2000) this is likely to be especially important for a climatologically diverse country such as China.

A number of researchers have developed multimedia models to investigate the fate of chemicals across large geographical regions in Europe and North America, such as EVn-BETR (Prevedouros et al., 2004), IMPACT 2002 (Margni et al., 2004) and BETR North America (MacLeod et al., 2001). Multimedia models perform an important role in risk assessment and decision support in Europe, e.g. Simplebox is embedded in EUSES (European Union System for the Evaluation of Substances) (Vermeire et al., 1997); CoZMo-POP2 is linked with a human food chain bioaccumulation model ACC-HUMAN in model CoZMoMAN to study the human exposure and body burden of PCBs for Baltic Sea drainage basin (Breivik et al., 2010; Quinn et al., 2011).

To date, as far as the authors are aware, there have been no attempts to develop a multimedia model for the whole of China for a broad range of substances including ionisable chemicals. Some multimedia fate models have been designed and applied for China but only in a local or a regional scale for neutral organic chemicals. For example, Mackay level III and IV fugacity models have been used to study the fate of benzo[a]pyrene, phenanthrene and γ-HCH in Tianjin by Tao et al. (Cao et al., 2004; Tao et al., 2003, 2006; Wang et al., 2002). Similar studies were completed in many other local or regional scale areas across China (Cao et al., 2007; Lang et al., 2007; Li et al., 2006; Xu et al., 2013; Zhang et al., 2013b).

This paper presents a Sino Evaluative Simplebox-MAMI Model (SESAMe) operating on two scales that is applicable for a broad range of ionisable and neutral chemicals. The model construct is presented and it has been used to investigate the influence of chemical and environmental properties on chemical P_{OV} and LRTP. It could be utilized further for human exposure estimation and environmental risk assessment for China. Simplebox 3.24a (Huijbregts et al., 2008) and a single box multimedia model MAMI III for ionisable chemicals (Franco and Trapp, 2010) have been referred to in constructing the model. Sobol sensitivity analysis method, instead of classic sensitivity analysis methods, has been used to quantify the importance of input variables on P_{OV} and LRTP. This method has been widely used in sensitivity analysis for hydrology models (Cibin et al., 2010; Tang et al., 2007a; Zhang et al., 2013a). The advantages of this method are that it considers a range of the input variables (Yang, 2011), which has not been considered by previous classical approaches (MacLeod et al., 2002); and it has been found to have the advantage of offering the most detailed description of the effect of a single parameter and its interactions with other parameters on the output, resulting in a more robust sensitivity ranking among the available global sensitivity analysis methods (Tang et al., 2007b), which is suitable for exploring the environmental–chemical interactions and influence on P_{OV} and LRTP. A series of neutral and acidic hypothetical chemicals have been used to study how representative environmental parameters influence P_{OV} and LRTP. Lastly, case studies using real chemicals have been conducted to explore the spatial variability of model output and how environmental properties affect P_{OV} and LRTP. These include benzo[a]pyrene (Bap), acenaphthene (ACE), triclosan (TCS) and dibenzofuran (DF) and enable a preliminary evaluation of the performance of the model.

2. Methods and materials

2.1. Model definition

SESAMe has been designed using the nested structure of Simplebox 3.24a model (Huijbregts et al., 2008) and the formulas developed in the MAMI III model (Franco and Trapp, 2010; Trapp et al., 2010) for modelling the concentration and fate of ionisable chemicals. The model has two scales; regional and continental, and considering that 200 km × 200 km has been the default size of regional scale for Europe in Simplebox, it was determined to be the size of the regional scale in this study. The continental scale was considered to be a 9,496,200 km^2 box covering the rest of the mainland China (Fig. S1 in Supplementary Information). The nested approach to spatial scale makes it possible to predict the concentration of chemicals both within the emission region and further afield and then to calculate P_{OV} and LRTP. Each scale contains 8 compartments including air, freshwater, sediment, natural soil, agricultural soil, urban soil, natural vegetation and agricultural vegetation. The chemical was assumed only to be emitted to the regional scale and fixed at 1 million tonnes per year. As in MAMI III model, only neutral molecules were assumed to volatilize to the air from water or soil compartments; unlike MAMI III model, the ideal condition was assumed in the water phase (ionic strength is 0). Vegetation was assumed to play an important role in the fate of airborne chemicals through deposition, so the vegetation compartment has been added for ionisable chemicals (acid, base and amphoter) to make the model complete (the calculations can be found in Supplementary Information, Eqs. (1–8)). In this study only acidic and neutral chemicals were included.

2.2. Environmental parameters

The spatial distribution maps of 14 environmental parameters were either collected from existing databases or generated from raw data taken from databases (Nos. 11–24 in Table 1 and Supplementary Information). ArcGIS 10 was used to extract the values of these parameters in order to represent each regional grid (Supplementary Information). The values of the variables for each of 267 grids completely within the boundary of mainland China were used to generate the environmental parameter database for the following hypothetical study.

2.3. Chemical parameters

To study the effect of environmental parameters on the model output, hypothetical chemicals were used: however, 130 real organic chemicals covering a wide range of chemical properties were taken from the substance database in Simplebox 3.24a model as chemical database, so that it would be easier to apply the results to real chemicals at a later date. The values for degradation rates and enthalpy of vaporization were updated or supplemented from the handbook of physicochemical properties (Mackay, 2005). The range of each parameter is contained in Table 1 (Nos. 1–10).

2.4. Persistence and LRTP

Chemical persistence is commonly represented by P_{OV}, and is the overall residence time (d) of the chemical in the environment (Iqbal et al., 2013). LRTP was calculated as the ratio of a chemical exported

Table 1
The physicochemical parameter and environmental parameter list.

No.	Variables	Unit	Range	Median[a]
1	Molecular mass	g/mol	72.1–545.6	201.2
2	Vapour pressure at 25 °C	Pa	1.1×10^{-10}–6.8×10^{4}	0.13
3	Water solubility at 25 °C	mol/m^3	1.6×10^{-10}–3.9×10^{2}	0.47
4	Enthalpy of vaporization	J/mol	2.6×10^{4}–1.2×10^{5}	6.4×10^{4}
5	Degradation half-lives in atmosphere	d	9.6×10^{-3}–2.9×10^{3}	2.29
6	Degradation half-lives in water	d	1.1×10^{-2}–2.5×10^{5}	20
7	Degradation half-lives in soil	d	1–2.1×10^{4}	60
8	Degradation half-lives in sediment	d	1–2.1×10^{4}	229.2
9	K_{OW}	–	5.4–1.8×10^{8}	1.3×10^{3}
10	pK_a for acidic chemical	–	2–10	5
11	Area fraction of nature soil[b]	–[c]	0.052–1	0.89
12	Area fraction of agriculture soil[b]	–	0–0.82	0.11
13	Area fraction of urban soil[b]	–	0–0.17	4.3×10^{-3}
14	Area fraction of fresh water[b]	–	0–0.11	4.5×10^{-3}
15	Area fraction of nature vegetation[d]	–	0–0.73	0.040
16	Temperature[e]	K	265.9–293.7	279.3
17	Wind speed[f]	m/s	1.05–4.23	2.43
18	Precipitation[e]	m/s	6.4×10^{-10}–6.0×10^{-8}	1.4×10^{-8}
19	Surface water depth[g,h]	m	0–5.97	0.87
20	Fraction of runoff[g]	–	0.21–0.36	0.27
21	Soil erosion rate[j]	m/s	0–2.0×10^{-10}	2.1×10^{-12}
22	Fraction of soil organic carbon[i]	–	0.0031–0.034	0.011
23	Surface water inflow[g]	m^3/s	0–28742	27
24	Surface water outflow[g]	m^3/s	0–29920.7	51.5

[a] It is the media value of the raw data for each parameter without transformation.
[b] http://www.geodata.cn.
[c] Dimensionless.
[d] http://www.iscgm.org.
[e] http://www.worldclim.org.
[f] http://www7.ncdc.noaa.gov, the interpolation method was used to generate the map by using the gauging values from the website.
[g] The surfacewater inflow, outflow and depth were from or calculated based on the surface water discharge map from Mick J. Whelan (Gandolfi et al., 1999; Whelan et al., 1999).
[h] The surfacewater depth was calculated from the surface water discharge (Allen et al., 1994; Schulze et al., 2005). The calculation method could be found in Supplementary Information.
[i] http://webarchive.iiasa.ac.at/Research/LUC/External-World-soil-database/.
[j] It was from the research of Doetterl et al. (Doetterl et al., 2012).

out of the emitting region to a surrounding region. The P_{OV} and LRTP were calculated by

$$P_{ov} = \frac{M_{tot}}{E}, \quad (1)$$

$$LRTP = 1 - \frac{M_R}{M_{tot}} \quad (2)$$

where M_{tot} is the total steady-state amount of a chemical (mol) in the (Chinese) environment, E is the emission rate (mol/day) and M_R is the steady-state amount of chemical in the emitting region (mol), which is the regional scale grid in this study. P_{OV} represents the chemical overall persistence in the Chinese environment and LRTP reflects the potential that chemicals transport out of the emission region. The closer the calculated LRTP value is to one, the higher the long-range transport potential is. The median values of all variables (Table 1) were used to study the effect of environmental parameters on P_{OV} and LRTP of chemicals with different physicochemical properties.

2.5. Sensitivity analysis

Model sensitivity analysis provides a method for understanding the relationship between input and output variables of a model by studying how the uncertainty in the result can be apportioned to uncertainty in input parameters (Saltelli et al., 2008). To identify the relative importance of input parameters on outputs by considering the parameter range, a global sensitivity analysis method, Sobol sensitivity analysis, has been used. This method was introduced by Sobol et al. (Archer et al., 1997; Sobol, 2001) and further developed by Saltelli (Saltelli, 2002). The sensitivity indices first-order index (S_i), second-order index (S_{ij}) and total-order index (S_{Ti}) were calculated (Eqs. (11)–(18) and more details are in the Supplementary Information). S_i indicates the sensitivity of the single ith parameter to the model output. S_{ij} represents the sensitivity of the interaction between the ith and the jth parameters, which reflects how important the combined effect of the two parameters is to the change in the output. S_{Ti} is the total sensitivity of the ith parameter contributed by the single ith parameter and its interactions with all other parameters. The sensitivity of single parameters or parameter interactions was assessed based on their contribution to the total variation caused by variance of all input variables. Sobol's sensitivity analysis indices were used to evaluate the influence of parameters to P_{OV} and LRTP. A larger index value represents a greater parameter effect taking into account the parameter range. A near-zero index does not, however, mean that there is little influence on model output from changing the parameter; it just suggests a lower contribution to the total output variability compared to the more important parameters considering the parameter range. The values of samples used in the Sobol's method were randomly taken from the environmental database and the chemical database (Sections 2.2 and 2.3), and two new databases were generated which included 24 parameters and 1000 samples respectively, so that enough samples were generated and extreme conditions could be included.

2.6. Hypothetical chemical and environmental parameter property space

For the estimation of P_{OV} and LRTP, hypothetical chemicals were utilized. K_{OW}, vapour pressure and pK_a were selected to study the interactive effect of environmental parameters and chemical properties on P_{OV} and LRTP. When analyzing the effect of a single parameter, other parameters were fixed at the median values taken from the chemical

database as shown in Table 1. The values selected for K_{OW}, vapour pressure and pK_a from the available range were the 10th, 50th and 90th percentiles of values for individual parameter in the chemical database. D_{OW} (octanol–water distribution coefficient) was used for ionizable chemicals calculated from K_{OW} values in the model.

The influence of climate parameters such as precipitation, wind speed and temperature, along with an environmental parameter, fraction of soil organic carbon contents (f_{OC}) as an important factor affecting the organic chemical partition, has been investigated with respect to P_{OV} and LRTP on chemicals with different values of K_{OW}, vapour pressure and pK_a. The spatial distribution of these parameters is shown in Fig. S7 in Supplementary Information. The 10th, 50th and 90th percentiles of values of the four environmental parameters from the database (Table S2) were used to study their effect to P_{OV} and LRTP.

2.7. Case study with Chinese environmental scenario and real chemicals

Following the hypothetical chemical study, real chemicals were considered in real Chinese environmental scenarios to explore the spatial variability of model output and how environmental properties affect P_{OV} and LRTP. The chemicals used were Bap and ACE, which are typically airborne chemicals, and TCS, which is mainly released into water. LRTP of the three chemicals was modelled across China. DF is used as an insecticide and also in industrial bleaching, so it is possible to be released into the air, water, agriculture soil and urban soil and its P_{OV} was modelled across China.

2.8. Emission scenarios

In order to provide a generic emission scenario, the sensitivity analysis of P_{OV} and LRTP assumed that the chemical was released into the air, water and three types of soil in equal amounts at the same time, which is represented as "AllE" emission scenario in this paper. When studying how the four environmental properties (Section 2.6) affect the fate of substances with different chemical properties, the AllE emission scenario was assumed for P_{OV} calculations; for LRTP calculations chemicals were assumed to be released entirely into the air or water, which were represented as "AirE" and "WE" emission scenario respectively, because they are transport media. Multimedia emissions for LRTP could be difficult to explain due to complex transport and removal processes. For real context case study, Bap and ACE were assumed as AirE and TCS was assumed as WE. DF was assumed to be released into the air (30%), water (30%), agricultural soil (20%) and urban soil (20%).

3. Results and discussion

3.1. Important parameters identified by sensitivity analysis

Figs. 1 and 2 show the parameter sensitivity indices of the P_{OV} for neutral (Figs. 1–2, a) and acidic (Figs. 1–2, b) chemicals, and the LRTP for neutral (Figs. 1–2, c) and acidic (Figs. 1–2, d) chemicals. In Fig. 1, the y-axis represents the first-order and total-order indices. The total height of bars shows the total-order index comprised of the first-order index (black bar) representing the individual parameter contribution and its interactive contributions (white bar) with all other parameters to the total variance. A higher total-order signifies that the parameter is more important than the other parameters considering the parameter range. A higher first-order index signifies that the contribution is greater from the individual parameter. The x-axis represents the parameter numbers, which are shown in Table 1. On the left side of the blue dotted line are chemical parameters, and on the right are environmental parameters. Fig. 2 indicates the interactive effect of any two parameters on P_{OV} and LRTP for both neutral and acidic chemicals.

The sensitivity analysis in Fig. 1 shows that chemical properties are more influential than environmental properties on P_{OV} and LRTP predictions for both neutral and acidic chemicals, which is the same as the conclusion made by Fenner et al. (Fenner et al., 2005) and some other researchers have also found chemical properties contribute more to

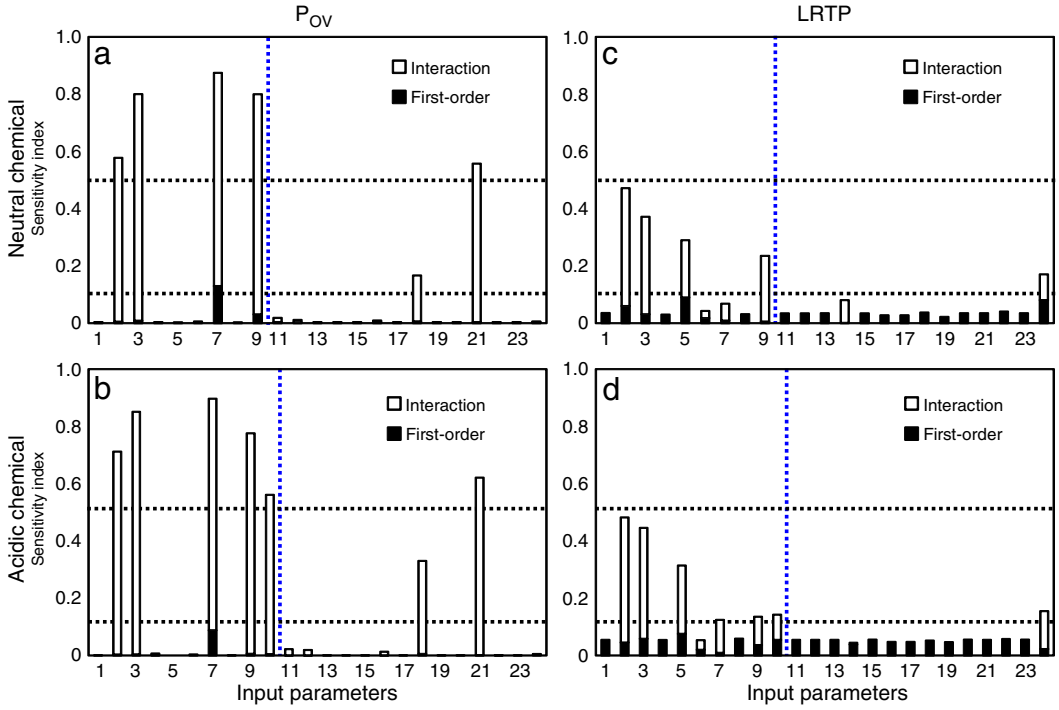

Fig. 1. The sensitivity indices of parameters on P_{OV} (a, b) and LRTP (c, d). The 24 input parameters are numbered in Table 1. On the left side of the blue dotted line are chemical parameters and on the right are environmental parameters. AllE is assumed.

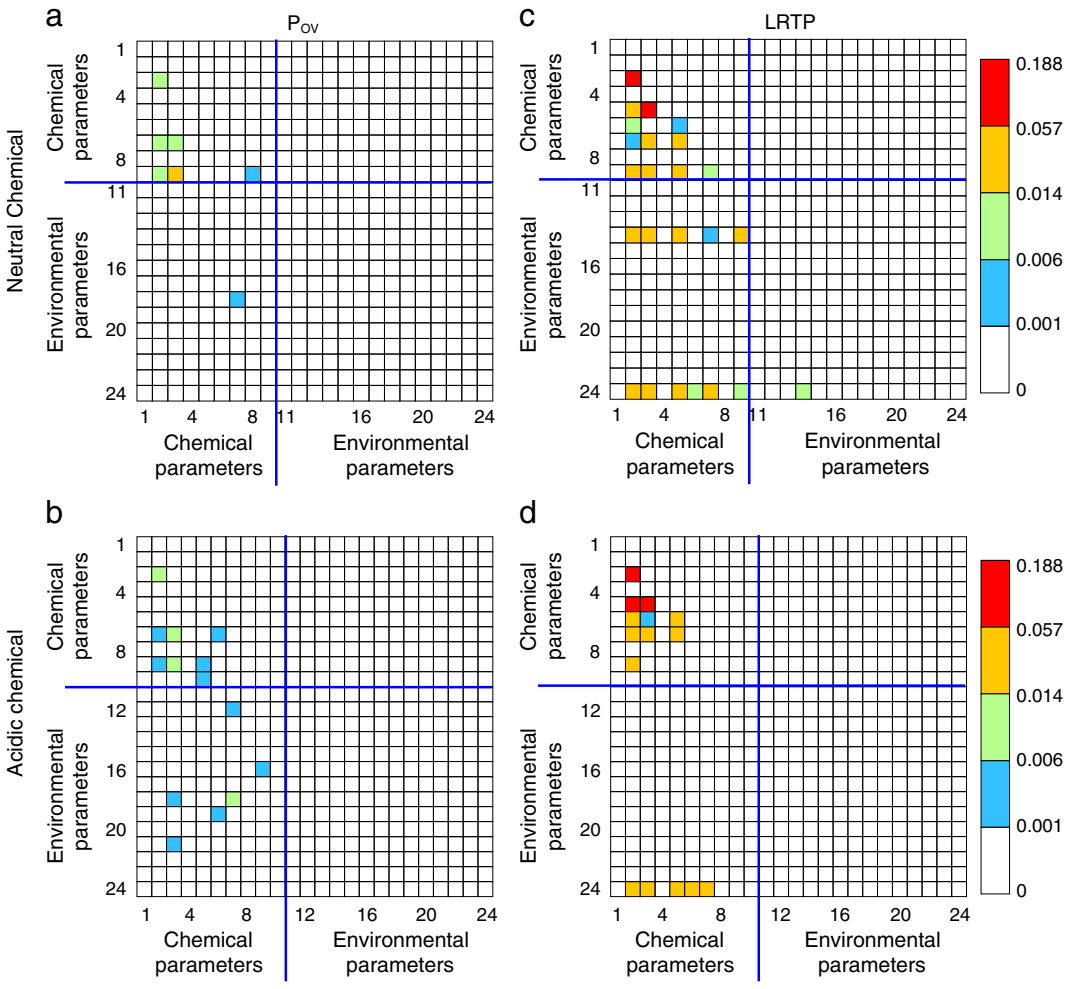

Fig. 2. Second-order indices for both the neutral and the acidic chemicals on P_{OV} (a, b) and LRTP (c, d). The parameter numbers are shown in Table 1. AllE is assumed.

concentration variation (Hollander et al., 2009). The chemical parameters which have a total-order index over 50% to P_{OV} are vapour pressure (2nd), water solubility (3rd), degradation half-life in soil (7th), K_{OW} (9th), and pK_a (10th for acidic chemicals) (Fig. 1a–b). The degradation half-life in soil is the most sensitive parameter to P_{OV}, as it is used for all three types of soil compartments and the degradation rate in vegetation is directly derived from it (Huijbregts et al., 2008), and it influences the chemical persistence in the soil compartment as a relatively stable medium. So the individual contribution to total P_{OV} variation from this parameter is also greater than the other parameters. For LRTP, besides the five chemical parameters, the degradation half-life in atmosphere (5th) also has a higher total-order index, as the air compartment is the major transport medium. Certain environmental parameters are also shown to be influential such as precipitation rates (18th) and soil erosion rates (21st) for P_{OV} and surfacewater outflow (24th) for LRTP. Soil erosion rate affects the flux of chemical transferring from soil to water, perhaps resulting in a reduction in chemical persistence, and the washout process by precipitation which transfers chemical from air to water, and especially to soil, can influence the overall persistence, so the two parameters are influential to P_{OV}. Surfacewater outflow provides the opportunity for chemicals to move far from the source region, so it is influential to LRTP.

For these parameters having higher total-order indices, interactive effects make a greater contribution. It means that when explaining the variation of the output led by changing one of these parameters, the individual parameter cannot be considered as the only cause but rather its combined effect with the other parameters. For those which have near-zero total-order indices, it only means they have a relative low effect on model output considering the parameter range, so if their values are varied, the model output may change. For P_{OV}, only the degradation half-life in soil has significantly higher first-order index compared to the other parameters. In contrast to P_{OV}, most chemical and environmental parameters have higher first-order indices for LRTP. Most total-order indices for P_{OV} and LRTP for acidic chemicals are higher than those of neutral chemicals, as K_{OC} values for acidic chemicals are smaller than those of neutral chemicals (Franco and Trapp, 2008). This is a result of more molecules of acidic chemicals being freely dissolved in soil or sediment pore water instead of being adsorbed and bound to solids.

It is observed in Fig. 2 that the interactive effect occurs mainly between chemical–chemical parameters and between chemical–environmental parameters, where there is a higher second-order index between chemical–chemical parameters. There is almost no interaction between environmental–environmental parameters except for area fraction of freshwater (14th) and surfacewater outflow (24th) for LRTP of neutral chemicals. The chemical–environmental parameter interactions are discussed further in the following sections. Three more influential chemical properties, vapour pressure, K_{OW}/D_{OW} and pK_a, were selected to study how environmental parameters affect the fate of chemicals with different chemical properties.

3.2. Effect of environmental parameters on chemicals with different K_{OW}, vapour pressure and pKa

In SESAMe, the transport media are water and air. Washout processes will generally decrease the LRTP as they reduce chemical concentrations in the air, however, the gas phase washout is not considered and precipitation has no influence on substances in the gas phase and only affects those adsorbed to aerosol particles. The soil and the sediment are considered as stable (non-transportable) media with lower degradation rates compared to air and water for most organic chemicals as shown in the literature, therefore, chemicals that tend to partition into soil and sediment compartments are likely to have relatively higher P_{OV} than those that tend to partition into air and water compartments. Removal processes and advective transport from the target environment out of the region are two main processes that decrease the P_{OV} of substances. Figs. 3–4 show how precipitation, temperature, wind speed and f_{OC} influence P_{OV} and LRTP of chemicals with different K_{OW}, vapour pressure and pK_a respectively. The three types of markers represent the chemical P_{OV} and LRTP with the 10th, 50th and 90th percentiles of values, respectively, for the individual environmental parameter in the environmental database. It should be noted that for the P_{OV} calculations AllE emission pathway is assumed whilst for LRTP AirE emission pathway is assumed. It is found that under different environmental conditions, P_{OV} doesn't change greatly with the increasing pK_a.

Fig. 3 shows that higher hydrophobicity increases chemical P_{OV}, as more hydrophobic chemicals are likely to be bound to organic carbon in soils and sediments and so become more persistent. The change of hydrophobicity has a smaller effect on acidic chemicals (pK_a at 5) due to their dissociation. As a result very hydrophobic neutral chemicals (K_{OW} around 1.3×10^6) are more persistent than acidic chemicals. Higher volatility decreases P_{OV} of chemicals (Fig. 3B), as more volatile chemicals tend to distribute in the air so that they can be advected out of the region. Variations in chemical acidity do not impact P_{OV} greatly compared to the changes in chemical hydrophobicity and vapour pressures.

It is indicated in Figs. 3 and S2 that compared to temperature, wind speed and f_{OC}, precipitation within the extent of the Chinese environment is more influential on P_{OV} especially for chemicals with lower K_{OW}/D_{OW}, vapour pressure and pK_a. Fig. S2 illustrates that the regional variation of temperature and the wind speed has limited effect to P_{OV} on chemicals with different properties. Precipitation and f_{OC} have more influence on chemicals with lower K_{OW}/D_{OW}, vapour pressure and pK_a. The difference of P_{OV} observed by changing the precipitation rate or f_{OC} whilst maintaining constant K_{OW}/D_{OW} or vapour pressure is slightly higher for acidic chemicals than for neutral chemicals. Generally, higher precipitation rates decrease P_{OV} due to the higher leaching and runoff processes which remove chemicals from the soil. The properties of lower K_{OW}/D_{OW} ($<1.3 \times 10^3/14$), lower vapour pressure (<0.13 Pa) or lower pK_a (<6) make chemicals more likely to partition to the water phase of the soil (Fig. S6B) and so precipitation decreases P_{OV} more for these chemicals. The f_{OC} has a slight effect on P_{OV} compared to precipitation and generally higher f_{OC} values will increase P_{OV} as it makes more chemicals bind onto solid matrices and become more persistent.

For LRTP with the AirE emission scenario, the combined effect of environmental parameters and chemical properties is more complex as shown in Fig. 4. Generally, wind speed is more influential than the other environmental parameters and higher wind speed can almost increase LRTP of chemical with different properties to the same extent; and the environmental parameters affect the LRTP of acidic chemicals to a greater extent than that of neutral chemicals; whether precipitation rates, temperature and f_{OC} affect LRTP replies on chemical properties.

Fig. 4 indicates that precipitation has a greater effect on LRTP of chemicals with high K_{OW}/D_{OW} than on LRTP of chemicals with low K_{OW}/D_{OW}. Higher precipitation rates decrease LRTP of chemical with high K_{OW}/D_{OW} but increase LRTP of chemicals with low K_{OW}/D_{OW}. Precipitation has a significant effect on chemicals with low vapour pressure at 1.7×10^{-5} Pa, and higher precipitation rates decrease their LRTP. No significant effect is shown on chemicals with higher vapour pressure (0.13 Pa and 4.5×10^3 Pa). It is easy to understand that chemicals

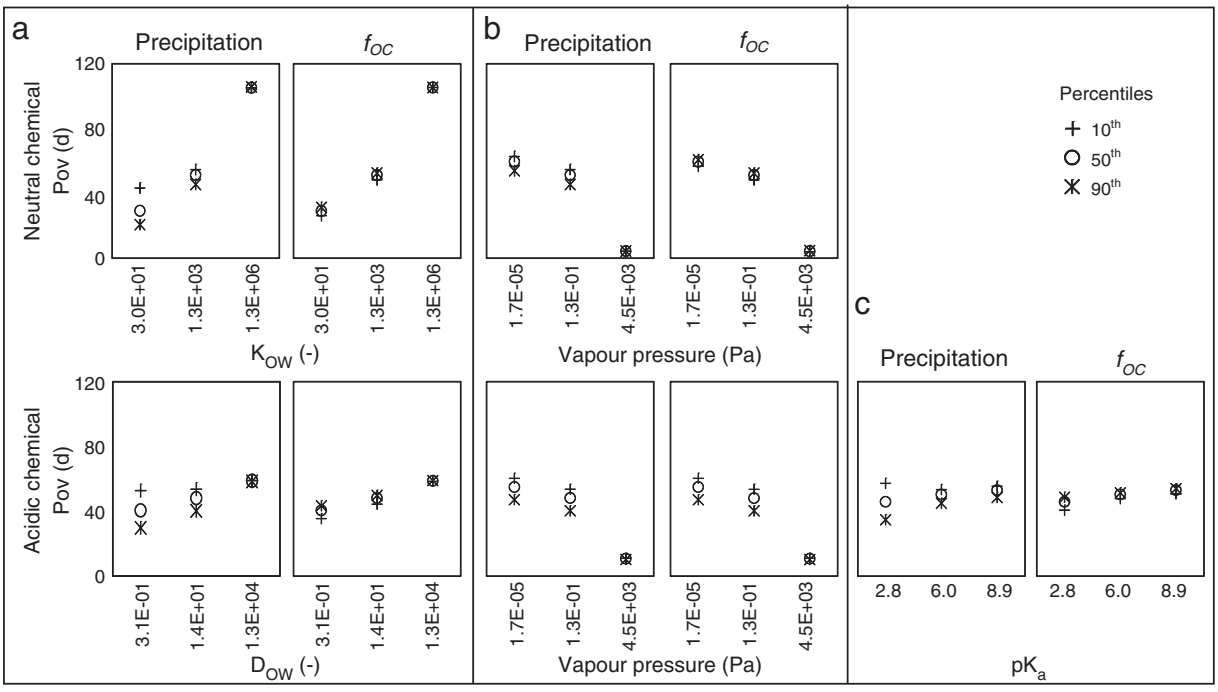

Fig. 3. The effect of precipitation and f_{OC} on P_{OV} for neutral and acidic chemicals with different K_{OW}/D_{OW} (A), vapour pressure (B) and pK_a (C); AllE emission way is assumed; the different markers represent P_{OV} with the 10th, 50th and 90th percentiles of values respectively for environmental parameters in Chinese environmental database.

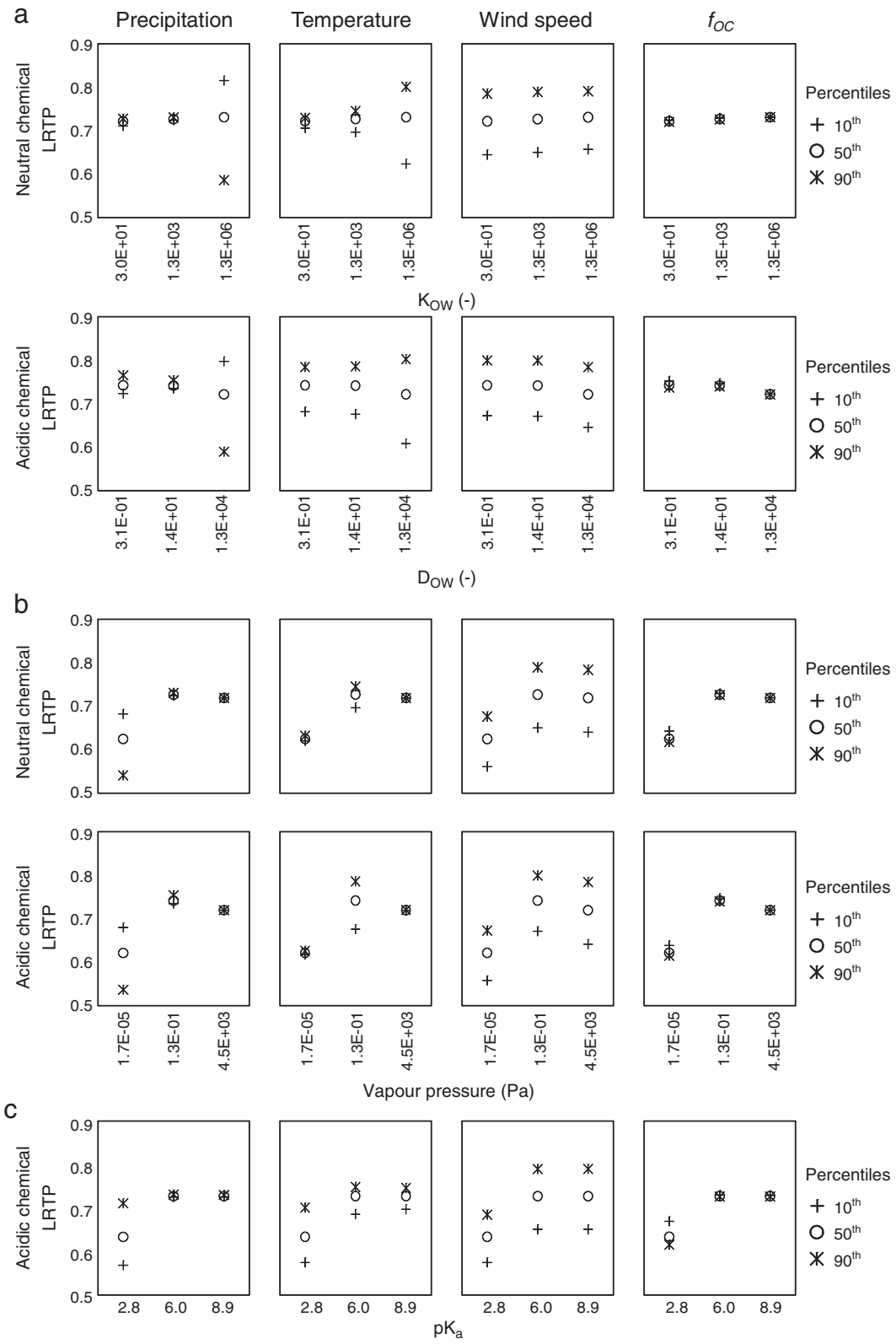

Fig. 4. The effect of precipitation, temperature, wind speed and f_{OC} on LRTP of neutral and acidic chemicals with different K_{OW}/D_{OW} (A), vapour pressure (B) and pK_a (C); AirE emission way is assumed; the different markers represent LRTP with the 10th, 50th and 90th percentiles of values respectively for environmental parameters in Chinese environmental database.

with high K_{OW}/D_{OW} and low vapour pressure are more likely to be adsorbed on aerosol particles after release into the air (Fig. S5A) and so more of them could be washed out by increasing the precipitation rates. Higher precipitation rates increase the LRTP largely for chemicals with lower pK_a at 2.8, whilst it has no significant effect on LRTP when pK_a is equal to or greater than 6 (Fig. 4C). This can be explained by the

pH assumption in most environmental compartments in this study (pH 5.8–7.5). When pK_a is under 6, most molecules exist in ionic form partitioning into soil and water compartments (Fig. S4A), so that the stronger runoff process moves more chemicals from soil to water when precipitation rate increases.

Fig. 4 shows that higher temperature increases LRTP as more chemicals partition into the air under higher temperatures where they can be advected to remote regions, although the extents of increase are different for chemicals with different properties. Temperature effects are more noticeable for chemicals with higher K_{OW}/D_{OW} than those with lower K_{OW}/D_{OW}; for chemicals with a median vapour pressure at 0.13 Pa than those with very high or low vapour pressure; and for higher acidic chemicals with pH at 2.8 than lower acidic chemicals. Chemicals with higher K_{OW}/D_{OW}, median vapour pressure (0.13 Pa) or higher acidity normally partially partition into the air and the other environmental compartments, so the variance of temperature within the Chinese environment is more likely to exert an influence on LRTP. Temperature has no significant effect on chemicals with vapour pressure at 1.7×10^{-5} Pa and 4.5×10^{3} Pa, as for highly volatile chemicals they are already present entirely in the air and for extremely low volatile chemicals, most of them tend not to partition into the air (Fig. S4A) and so the variance of temperature is unlikely to affect significantly the partition for these chemicals.

f_{OC} exhibited a slight effect on LRTP as shown in Fig. 4. Higher f_{OC} decreases LRTP, although the effect is not significant on chemicals with high K_{OW}/D_{OW} ($\geq 1.3 \times 10^3/14$), high vapour pressure ($\geq$0.13 Pa) and for high pK_a ($\geq$6). It is understandable that higher f_{OC} makes more chemicals bind onto solid matrices and become more persistent and thus reduce transport distances. Chemicals with high K_{OW}/D_{OW}, vapour pressure and pK_a are more likely to bind on solids matrices so that the f_{OC} will not affect their partitioning and fate significantly.

For LRTP with WE scenario, precipitation and f_{OC} don't have significant effect on chemicals with different properties (Fig. S3); higher wind speeds only increase the LRTP for extremely volatile chemicals (vapour pressure is 4.5×10^3 Pa) and higher temperature only increases the LRTP for extremely volatile acids, whilst they do not have significant effects on LRTP for the other chemicals in Fig. S3. This is because most chemicals may stay in the water after being released except for those that are highly volatile chemicals. Therefore, the parameters related to the water phase, such as surfacewater discharge and area fraction of surfacewater, may be vital factors to affecting LRTP for waterborne chemicals, which will be shown in the following real chemical study with the Chinese environment.

3.3. Case study with Chinese environmental scenario

When placing the above findings into context for real Chinese environmental scenarios (Fig. S7–S9) and real substances, chemicals that are very hydrophilic or have low volatility may be more persistent in the northwest i.e. Xinjiang province than in the southeast e.g. Fujian and Guangdong provinces, assuming multimedia release pattern due to the higher precipitation rates in southeast (Fig. S7a). These differences could be greater for ionizable chemicals. Chemicals may exhibit greater persistence in Heilongjiang, Jilin, northeast of Inner Mongolia in the northeast, the adjacent boundary area of Qinghai, Gansu and Sichuan provinces in the west, northwest of Xinjiang, and in most area of Tibet with AllE pattern due to high f_{OC} in these areas (Fig. S7d). However, for an extremely hydrophobic or highly volatile chemical, persistence may not vary that much across the whole of China. For example, PBDEs exhibit low volatilities and high hydrophobicity especially the isomers with more bromines, so they are very persistent in all environments with little difference across China. The coefficients of variation (CV) are only 0.057 and 0.049 for BDE-47 and BDE-153, which are quite small compared to 0.176 for DF. The distribution of P_{OV} for DF in China is shown in Fig. 5, in which DF has the highest persistence in northwest of Xinjiang, part of Gansu, northeast of Inner Mongolia, Heilongjiang and Jilin, as these areas have higher f_{OC}. Although the f_{OC} in Tibet is also high, most area in Tibet is natural soil without DF emission.

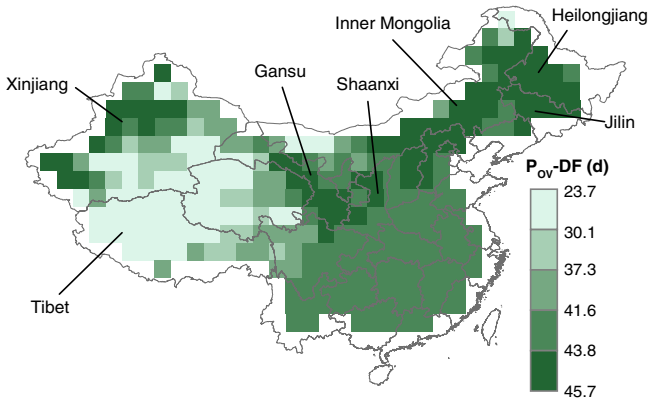

Fig. 5. P_{OV} distribution of Dibenzofuran (DF). DF is assumed to be released into the air (30%), water (30%), agricultural soil (20%) and urban soil (20%).

Chemicals with low pK_a values when released across all media are always more persistent in the northwest becoming less persistent when moving to the southeast as a result of increased precipitation. They may also be more persistent in those areas with high f_{OC} stated above, however P_{OV} of chemicals with stronger acidity have greater variance than that of chemicals with weaker acidity. Therefore, the P_{OV} of an acid like TCS ($pK_a = 7.9$), in Xinjiang is about 1.5 times of that in Southeast (e.g. Fujian, Guangdong, Jiangxi and Zhejiang provinces) due to the lower precipitation rates in Xinjiang.

For LRTP under the AirE scenario, the situation is more complex as more environmental factors are important. For very hydrophobic and low volatility chemicals like Bap, temperature has little effect. If released to south Xinjiang or west Inner Mongolia the LRTP of Bap is relative high (Fig. 6a) due to low precipitation, whilst it could be lower if released to large areas of the south of China especially to Sichuan and Chongqing due to high precipitation rates and low wind speeds, and the difference of LRTP for Bap could be about 0.46 between the two regions. Compared to Bap, for chemicals with lower hydrophobicity and higher volatility like ACE, the effect of precipitation on LRTP is not significant but temperature and wind speed are more influential. Fig. 6b shows that LRTP of ACE is the highest if released to Tibet, west of Qinghai and some regions in Inner Mongolia, whilst it is the lowest if released to most area of Sichuan and Chongqing. This aligns very well with the wind speed map in Fig. S7c. The greatest LRTP difference could be about 0.18 between regions.

LRTP of TCS is calculated across China with WE scenario. The spatial variation of LRTP is much greater than that of Bap and ACE, as it is highly related to the properties of water compartment since TCS has a rather low vapour pressure. As shown in Figs. 7 and S9, LRTP of TCS matches well with the surfacewater outflow of grids. It is higher if TCS is released to areas with abundant water and higher water discharge (outflow), such as Yellow River and Yangtze River catchments, southeast of China with abundant water catchments, northeast where there is Songhua River catchment and part of Xinjiang.

4. Conclusions

This study focuses on constructing a multimedia model capable for a wide range of neutral and ionizable chemicals covering the whole of China and applying it to estimate chemical P_{OV} and LRTP. The influence of environmental parameters to P_{OV} and LRTP has been carefully studied with the combination of effect from chemical properties. The sensitivity analysis shows that physicochemical properties are more influential to the model output, however, certain environmental parameters are also important. Interactive effects make a greater contribution rather

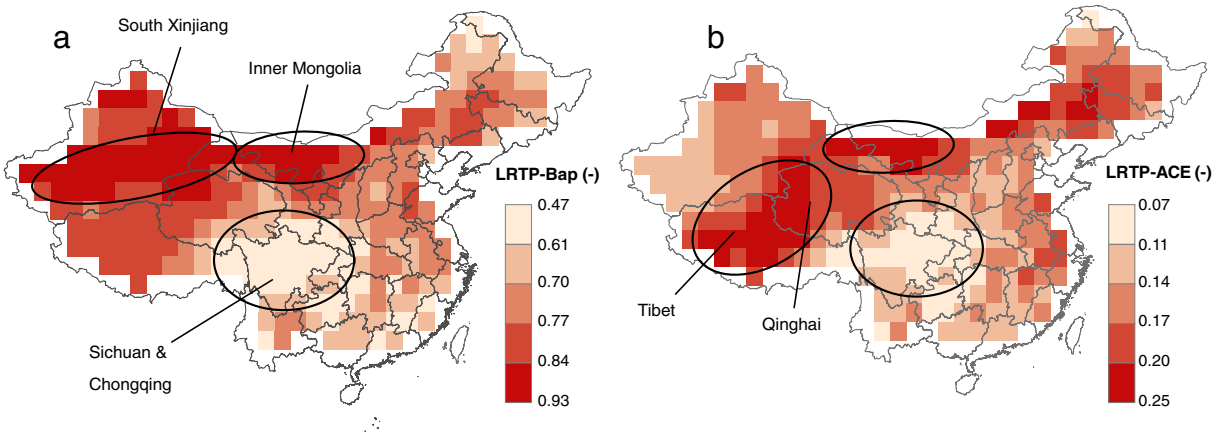

Fig. 6. LRTP of benzo[a]pyrene (Bap, a), acenaphthene (ACE, b) across China. Bap and ACE are assumed as AirE.

than individual parameters to variation of model results. Interactive effects occur mainly between chemical–chemical parameters and between chemical–environmental parameters, but not between environmental–environmental parameters.

Hypothetical chemicals and emission data are used to investigate the effect of four environmental parameters on P_{OV} and LRTP of chemicals with different physicochemical properties. Generally, for P_{OV}, precipitation is more influential than other environmental parameters, whilst temperature and wind speed do not contribute significantly to P_{OV} variation; for LRTP, wind speed is more influential than the other environmental parameters and higher wind speed always increases LRTP of chemicals with different properties to the same extent. The effects of other environmental parameters rely on their interactive effects with chemical properties. f_{OC} has a slight effect on P_{OV} and LRTP, and higher f_{OC} always increases P_{OV} and decreased LRTP. Based on the conclusions from hypothetical studies above, rough estimations could be made by comparing P_{OV} and LRTP of a specific chemical among the regions according to the chemical and environmental properties.

The model performance has been evaluated using real chemical case studies. DF released into the air, water, urban and agricultural soils has higher P_{OV} in northwest of Xinjiang, part of Gansu, northeast of Inner Mongolia, Heilongjiang and Jilin, which have higher f_{OC}. Bap and ACE, released into the air, have different LRTP distribution across China, as the vital environmental parameters are different due to different chemical properties. LRTP of Bap is relatively high if released in south Xinjiang and west Inner Mongolia; LRTP of ACE is relatively high if released in Tibet and west Inner Mongolia. TCS released into water has higher LRTP in Yellow River and Yangtze River catchments, where the water discharge is relatively high. This kind of information may be useful for determining the sensitive regions in China for future chemical monitoring and research.

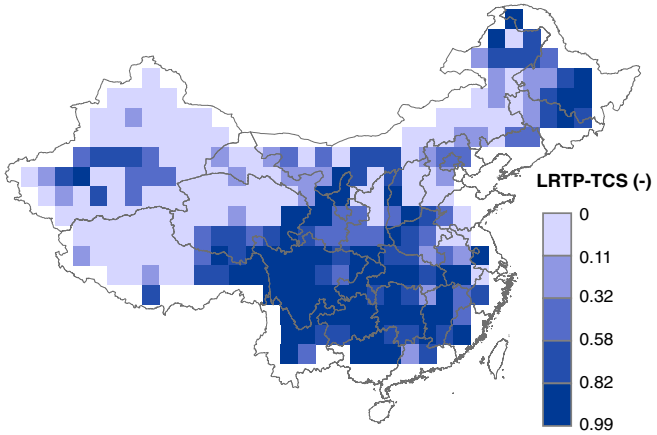

Fig. 7. LRTP of triclosan (TCS) across China. TCS is assumed as WE.

Additional research could focus not only on screening and risk assessment of chemicals across China by using this model to estimate P_{OV} and LRTP, but also on improving the model parameterisation to enable more accurate predictions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.envint.2014.03.020.

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Supporting information for

A new multimedia contaminant fate model for China: how important are environmental parameters in influencing chemical persistence and long-range transport potential?

Ying Zhu[1], Oliver R. Price[2], Shu Tao[3], Kevin C. Jones[1] and Andy J. Sweetman[1*]

[1] Centre for Chemicals Management, Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, United Kingdom

[2] Safety and Environmental Assurance Centre, Unilever, Sharnbrook MK44 1LQ, United Kingdom

[3] College of Urban and Environmental Sciences, Peking University, Beijing 100871, China

Model definition

The definition of regional scale and continental scale and the environmental compartments included in the model are shown in Fig. S1.

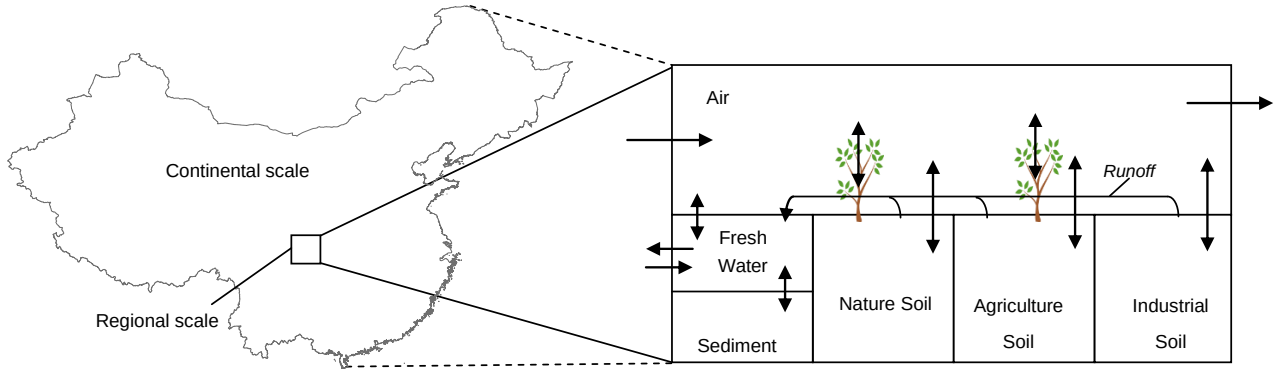

Fig. S1. Nested structure of SeSaME for China; regional scale is 200 km × 200 km; continental scale is 9,496,200 km^2

SeSeME has been designed capable for ionizable chemicals with considering vegetation compartment. MAMI III doesn't have the vegetation compartment, so the method in this study is provided here.

The mass balance equation for vegetation compartment:

$$\frac{dm_{veg}}{dt} = diffusion_{air-veg} + deposition_{air-veg} + transpiration_{soil-veg} - diffusion_{veg-air} - litterflow_{veg-soil} - degradation - harvest$$

There is not direct input to vegetation compartment.

Air-vegetation diffusion:

$$\frac{dm_{diffveg}}{dt} = P_{air-veg} \cdot a_{air} \cdot \varphi_{n,air} - P_{veg-air} \cdot a_{veg} \cdot \varphi_{n,veg} \quad (1)$$

Dry and wet deposition from air to vegetation:

$$\frac{dm_{dep_{air-veg}}}{dt} = Area_{veg} \cdot (V_{dep,dry} + V_{precipitation} \cdot \varepsilon_{coll}) \cdot a_{air} \cdot (B_{aerosol,Water} + B_{aerosol,Solid}) \quad (2)$$

Transpiration from soil to vegetation

$$\frac{dm_{transpiration}}{dt} = Area_{veg} \cdot Q_{veg} \cdot TSCF_{veg} \cdot a_{soil} \cdot (B_{soil,air} + B_{soil.water}) \quad (3)$$

Litter flow from vegetation to soil:

$$\frac{dm_{litter}}{dt} = (1 - harvest) \cdot Growth_{veg} \cdot Volume_{veg} \cdot a_{veg} \cdot B_{veg} \quad (4)$$

Harvest flow:

$$\frac{dm_{harvest}}{dt} = harvest \cdot Growth_{veg} \cdot Volume_{veg} \cdot a_{veg} \cdot B_{veg} \quad (5)$$

Degradation:

$$\frac{dm_{deg}}{dt} = Volume_{veg} \cdot kdeg_{veg} \cdot a_{veg} \cdot B_{veg} \quad (6)$$

$\varphi_{n,j}$ was the fraction of neutral species in j compartment, while a_j was the activity in j compartment (Franco and Trapp 2010). B (m^3m^{-3}) was the "apparent bulk activity capacity" of the compartment (Trapp et al. 2010). All B_j calculation above could be found in Franco and Trapp's paper (Franco and Trapp 2010) except the total apparent bulk activity capacity for vegetation B_{veg}. B_{veg} was calculated as equation (7) below (Trapp et al. 2010). Different with MAMI III, the ideal condition was assumed in the water phase (ionic strength is 0), so the activity coefficient is 1 for all $B_j$calculation including in equation (7) for SeSaME. $P_{air,veg}$ in equation (1) was the mass transfer coefficient air-vegetation (m/s), which referred to Simplebox 3.24a (Huijbregts et al. 2008). ε_{coll} in equation (2) was particle collection efficiency of rain (-); $V_{dep,dry}$ was the aerosol dry deposition velocity (m/s) and $V_{precipitation}$was the precipitation rate (m/s). In equation (3), Q_{veg} was the water absorption rate of vegetation from soil (m/s); $TSCF_{veg}$ was transpiration stream concentration factor (-). In equation (4) and (5), "$harvest$" was the harvesting efficiency for vegetation (-). For natural soil, it was assumed as 0. $Growth_{veg}$ was vegetation growth rate (s^{-1}). In equation (6), $kdeg_{veg}$ was the chemical degradation rate in vegetation (-). It was derived from the degradation rate in soil, which was $kdeg_{veg} = 17 \cdot kdeg_{soil}$(Huijbregts et al. 2008).

The total apparent bulk activity capacity for vegetation:

$$B_{veg} = W_{veg} \cdot \left(\varphi_{n,vegwater} + \varphi_{i,vegwater}\right) + \mathrm{DryMass}_{veg}(\varphi_{n,vegDryMass} \cdot Kd_n + \varphi_{i,vegDryMass} \cdot Kd_i) \quad (7)$$

W_{veg} was the volume fraction of water in vegetation (0.8 for natural vegetation and 0.85 for agricultural vegetation, same as in Simplebox 3.24a); $\mathrm{DryMass}_{veg}$was the volume fraction of dry mass part in vegetation. $\varphi_{n,vegwater}$ and $\varphi_{i,vegwater}$ were faction of neutral and ionic species in the water of vegetation; $\varphi_{n,vegxylem}$ and $\varphi_{i,vegxylem}$ were fraction of neutral and ionic species in the dry mass of vegetation. Kd was the solid-water sorption coefficient for neutral (Kd_n) and ionic (Kd_i) species (Franco and Trapp 2010), but here the solid is the dry mass of vegetation. So it was calculated as below:

$$Kd = K_{OC} \cdot \rho_{veg} \cdot f_{lipid} \quad (8)$$

K_{OC} was the octanol-water partition coefficient of neutral or ionic molecules. ρ_{veg} was the density of vegetation. f_{lipid} was the fraction of lipid in dry mass.

Environmental parameters preparing

14 environmental variables were collected or generated from the raw data taken from databases for this model in the study. Daily monitoring wind speed data from 713 gauging stations across and around the boundary of China were downloaded from the database of NOAA Satellite and Information Service (http://www7.ncdc.noaa.gov/CDO/cdo) for about 60 years. The years having completed records for 12 months were selected and at least 10 days' complete record for one month was required when selecting. IDW (Inverse distance weighting) interpolation method has been used in ArcGIS 10.0 to generate the continuous map for wind speed covering China by using the gauging raw data.

The surface water depth is calculated based on the surface water discharge as below:

$$\mathrm{w} = \alpha \cdot Q^{\beta} \quad (9)$$

$$\mathrm{d} = w^{-3/5} \cdot Q^{3/5} \cdot J^{-3/10} \cdot n^{3/5} \quad (10)$$

where w is surface water width (m), and from Allen et al. (Allen et al. 1994), α is 2.71 and β is 0.557. Q is the discharge (m^3/s); d is depth (m); J is channel slope (m/m) and n is river bed roughness (-), which is 0.045 as a representative value (Pistocchi and Pennington 2006).

Maps of most parameters are 1 km resolution except for discharge map which is 50 km resolution. The values of all 11-22 parameters in table 1 for each 200 km × 200 km grid are extracted in ArcGIS. A fishnet map with 200 km × 200 km grids covering China has been created in ArcGIS. "Zonal statistics" tool in ArcGIS has been used to calculate the average value of 1km pixels in each 200 km × 200 km grid with the fishnet map and environmental parameter map as input. Surface water inflow and outflow values for each grid were calculated manually from discharge map in ArcGIS with Chinese major river map to identify the location of rivers and elevation map to identify the flow direction.

Chemical properties for real chemicals

Table S1. Chemical properties for real chemicals used in the case study

	Molecular weight	Vapour pressue (25 ˚C)	K_{OW}	kdeg(air)	kdeg(water)	kdeg(sed)	kdeg(soil)	pKa
	$g.mol^{-1}$	Pa	-	s^{-1}	s^{-1}	s^{-1}	s^{-1}	-
Dibenzofuran	168.2	3.0E-01	2.0E+04	3.5E-06	1.1E-06	3.5E-08	1.1E-07	-
BDE-47	485.8	1.87E-04	3.55E+06	7.52E-07	5.35E-08	1.34E-08	5.35E-08	-
BDE-153	643.6	2.09E-06	4.17E+07	1.73E-07	5.35E-08	1.34E-08	5.35E-08	-
Benzo(a)pyrene	252.3	7.00E-07	1.10E+06	1.13E-06	1.13E-07	3.50E-09	1.13E-08	-
Acenaphthene	154.2	2.87E-01	8.32E+03	7.70E-05	1.28E-06	2.08E-07	1.48E-07	-
Triclosan	289.5	6.93E-04	6.31E+04	8.02E-06	1.34E-07	1.49E-08	6.69E-08	7.9

Sobol sensitivity analysis

Sobol sensitivity analysis method provides a method quantifying the importance of input variables to model output taking into account the range of variables. The classic sensitivity analysis method normally used in environmental model doesn't have such advantage. Equations 3 – 10 show how to calculate the indices of sobol's sensitivity analysis.

First-order index $S_i = \frac{D_i}{D}$ (11)

Second-order index $S_{ij} = \frac{D_{ij}}{D}$ (12)

Total-order index $S_{Ti} = 1 - \frac{D_{\sim i}}{D}$ (13)

Where D was the total variation; D_i was the variation due to the single ith parameter, and D_{ij} was the amount of variation caused by the interaction between the ith and jth parameters, and $D_{\sim i}$ was the variation due to all other parameters except the ith parameter. S_i indicated the sensitivity of the ith parameter to the model output. S_{Ti} was the total sensitivity of ith parameter contributed by the single ith parameter and its interaction with all other parameters. S_{ij} refers to the sensitivity of the interaction between the ith and jth parameter, which reflects the contribution to the variation of outputs by change of the two parameters. In this analysis, two parameter databases A and B were needed. Each of the two databases included all 24 input parameters and 1000 samples (24 × 1000 matrix). The 1000 values of each parameter were randomly taken correspondingly from the real chemical database (130 chemicals) and the Chinese environmental database (267 grids).

$$f_0 = \frac{1}{n} \sum_{s=1}^{n} f(\theta_s^a) \quad (14)$$

$$D = \frac{1}{n} \sum_{s=1}^{n} f^2(\theta_s^a) - f_0^2 \quad (15)$$

$$D_i = \frac{1}{n} \sum_{s=1}^{n} f(\theta_s^a) f(\theta_{(-i)s}^b, \theta_{is}^a) - f_0^2 \quad (16)$$

$$D_{ij} = \left[\frac{1}{n} \sum_{s=1}^{n} f(\theta_s^a) f(\theta_{(-i,-j)s}^b, \theta_{(i,j)s}^a) - f_0^2 \right] - D_i - D_j \quad (17)$$

$$D_{-i} = \frac{1}{n} \sum_{s=1}^{n} f(\theta_s^a) f(\theta_{(-i)s}^a, \theta_{is}^b) - f_0^2 \quad (18)$$

Where θ_s^a was the parameter vector from database A, and s meant individual sample. $f(\theta_s)$ was the goodness-of-fit metric of model output. θ_{is}^a and θ_{is}^b meant the ith parameter was sampled from database A and database B respectively. $\theta_{(-i)s}^a$ and $\theta_{(-i)s}^b$ meant parameters were sampled from respectively database A and B without the ith parameter. $\theta_{(i,j)s}^a$ represented that the ith and the jth parameters were both sampled from database A. $\theta_{(-i,-j)s}^b$ represented that all parameters were taken from database B except for the ith and the jth parameters. The equation (5) - (8) were the Monte Carlo estimation of the decomposed terms of total variance.

Effect of environmental parameters on chemicals with different K_{OW}, vapour pressure and pK_a

Table S2. the values of 10th, 50th and 90th percentiles of four environmental parameters

	10th percentile	50th percentile	90th percentile
Precipitation rate (m/d)	1.4E-04	1.2E-03	3.6E-03
Temperature (˚C)	-3.8	6.1	16.3
Wind speed (m/s)	1.69	2.43	3.44
f_{oc} (%)	0.56	1.08	1.57

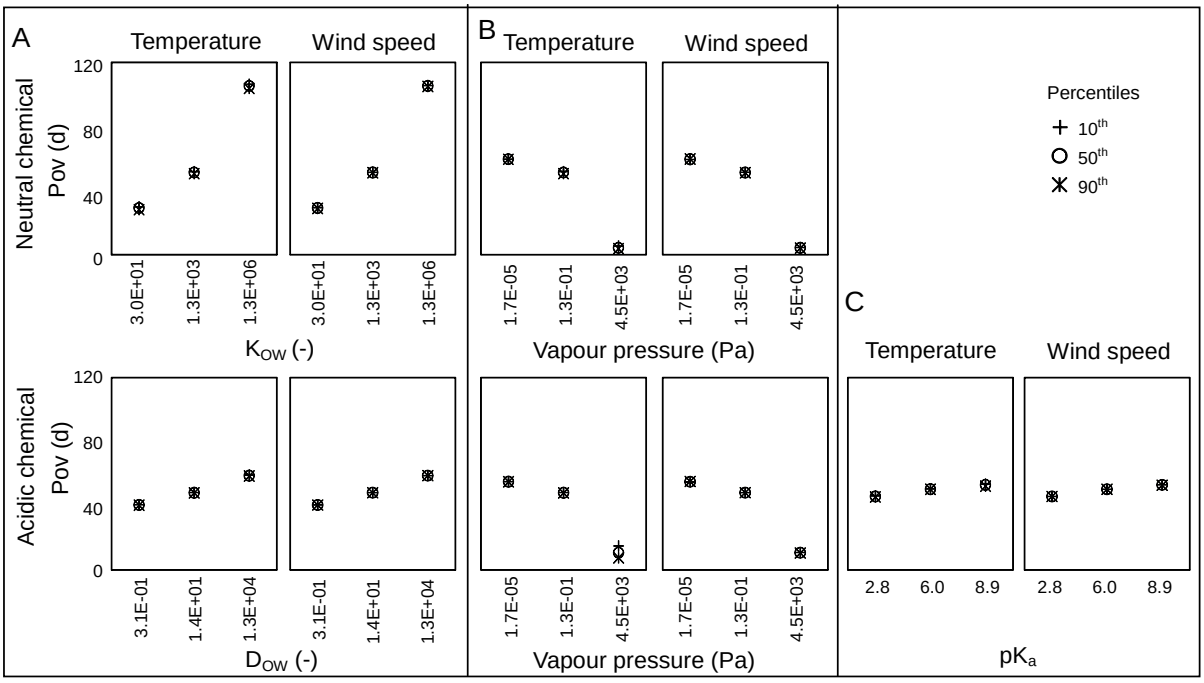

Fig. S2. The effect of temperature and wind speed on P_{OV} for neutral and acidic chemicals with different K_{OW}/D_{OW} (A), vapour pressure (B) and pK_a (C); AllE emission way is assumed; the different markers represent P_{OV} with the 10^{th}, 50^{th} and 90^{th} percentiles of values respectively for environmental parameters in Chinese environmental database.

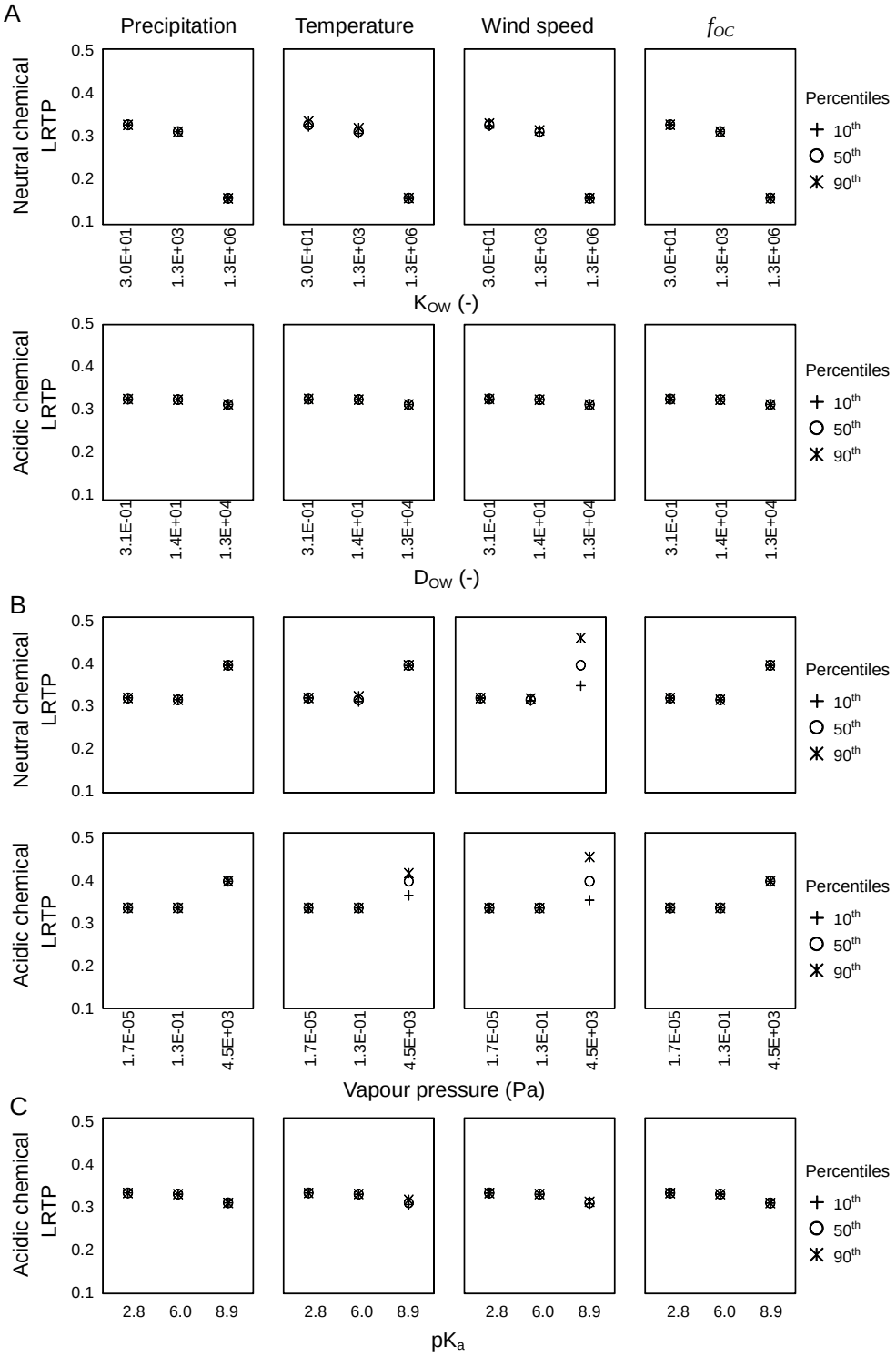

Fig. S3. The effect of precipitation, temperature, wind speed and f_{OC} on LRTP of neutral and acidic chemicals with different K_{OW}/D_{OW} (A), vapour pressure (B) and pK_a (C); WE emission way is assumed; the different markers represent LRTP with the 10th, 50th and 90th percentiles of values respectively for environmental parameters in Chinese environmental database.

Chemical partition in sub-phase in air and soil compartments

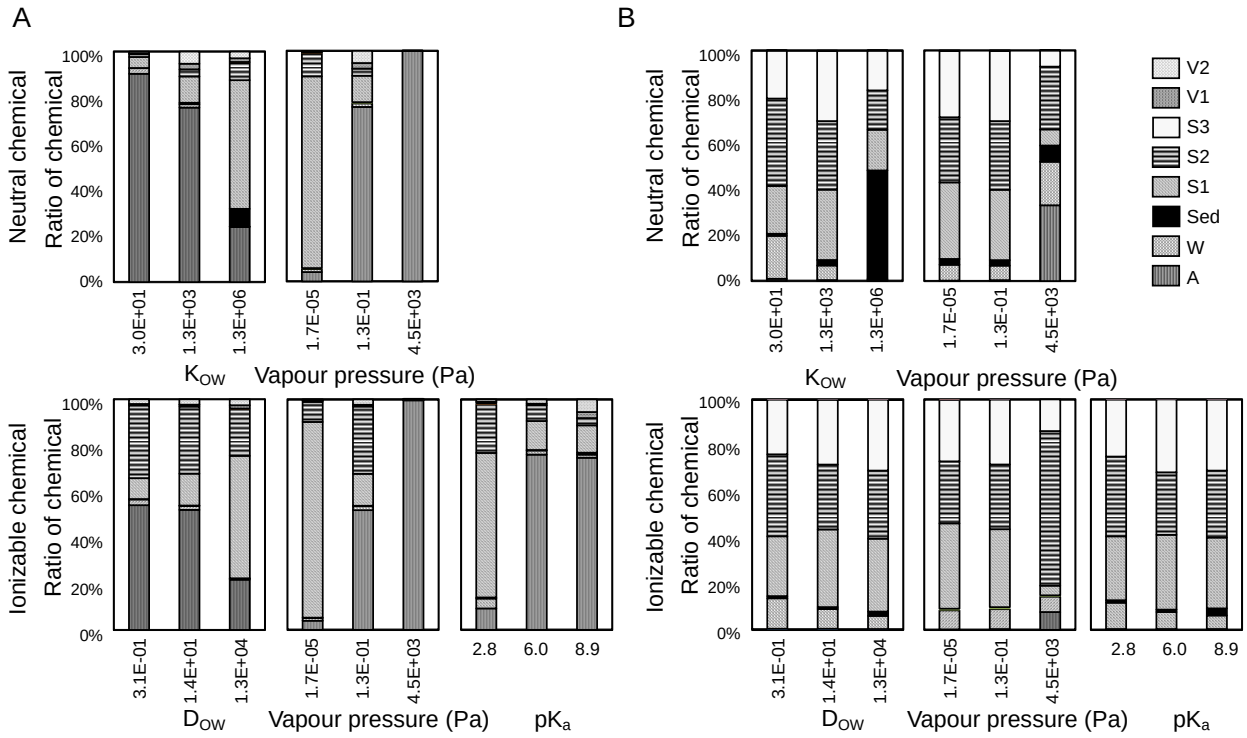

Fig. S4. The distribution of chemicals with different K_{OW}/D_{OW}, vapour pressure and pK_a in environmental compartments with median values as environmental parameters; A, the chemical is released to air; B, the chemical is released equally to air, soil, water and sediment. Legend: A - air; W - water; Sed - sediment; S1- natural soil; S2 - agricultural soil; S3 - urban soil; V1 - natural vegetation; V2 - agricultural vegetation.

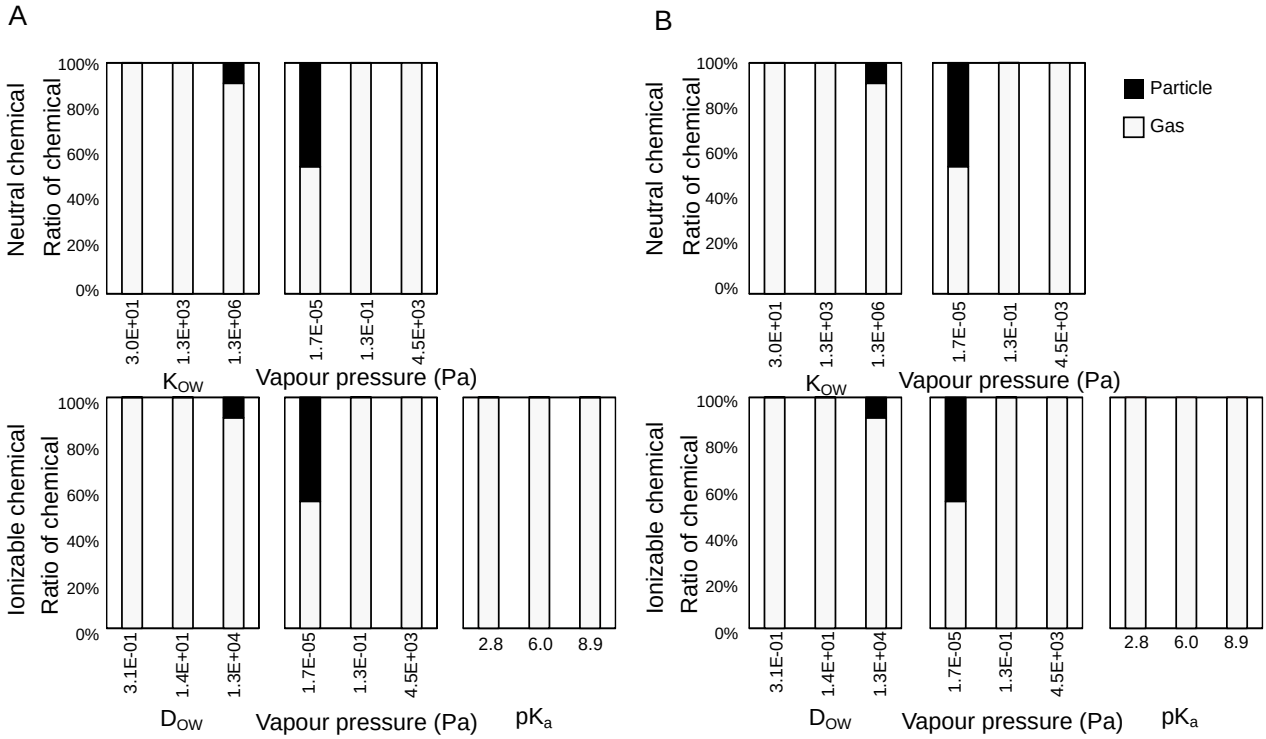

Fig. S5. Partition between gas and aerosol particle phases in atmosphere of chemical with different K_{OW}/D_{OW}, vapour pressure and pK_a; A, the chemical is released to air; B, the chemical is released equally to air, soil, water and sediment

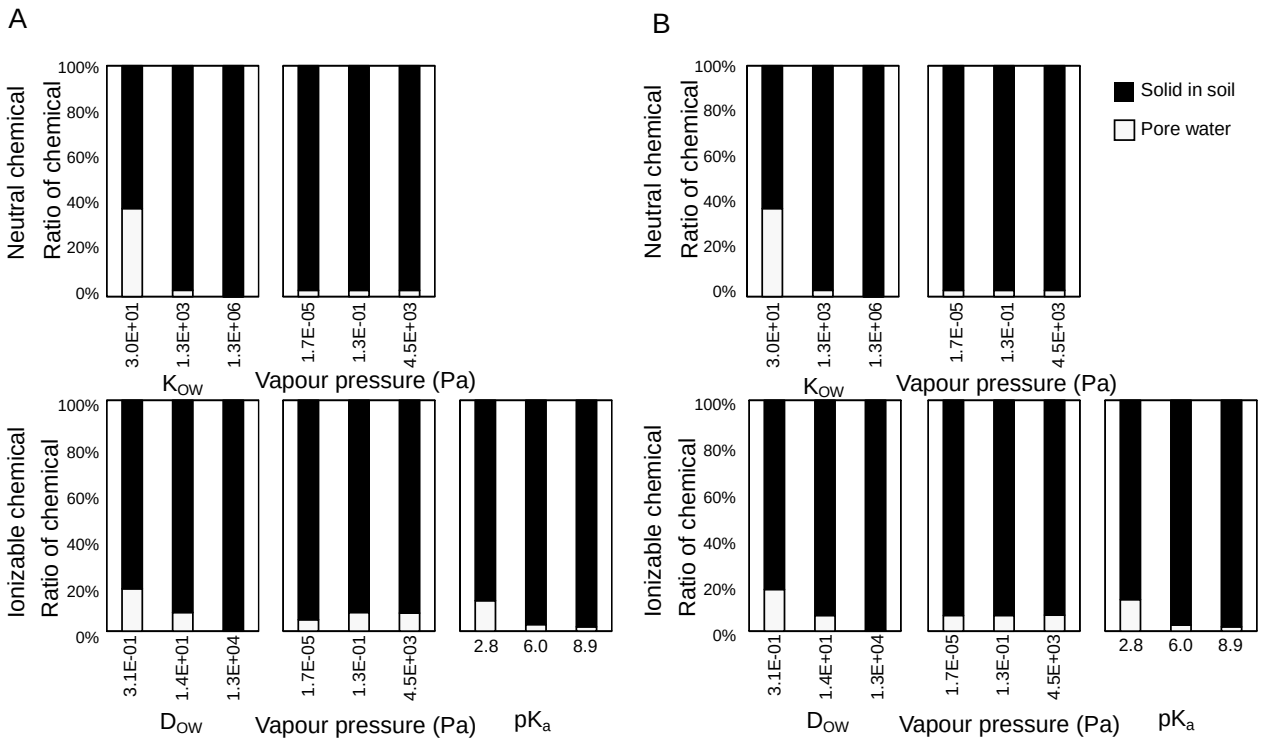

Fig. S6. Partition between pore water and solid in soil of chemical with different K_{OW}/D_{OW}, vapour pressure and pK_a; A, the chemical is released to air; B, the chemical is released equally to air, soil, water and sediment

The spatial distribution of four environmental parameters

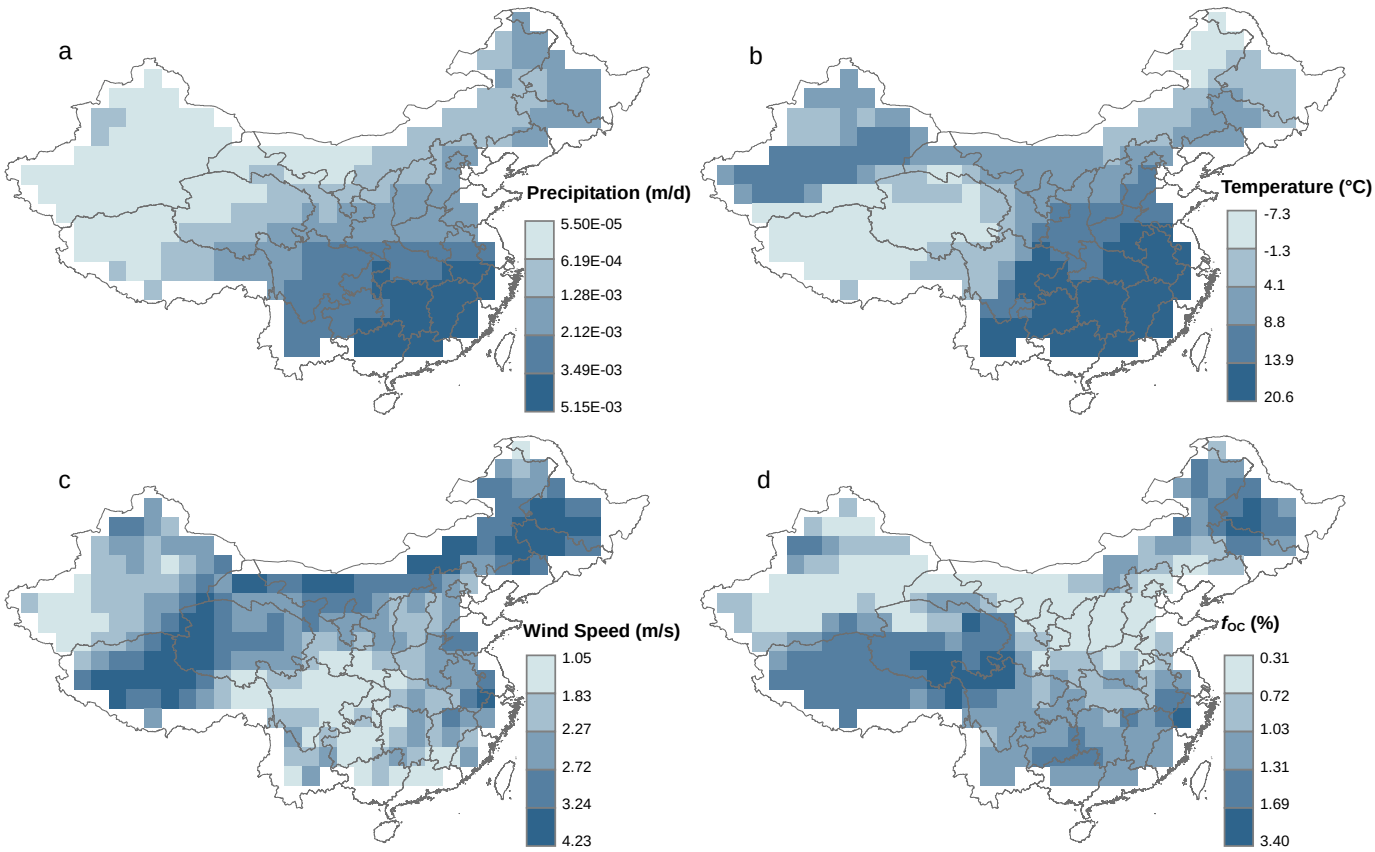

Fig. S7. Maps of precipitation, temperature, wind speed and fraction of soil organic carbon contents for 267 200 × 200 km^2 grids in China

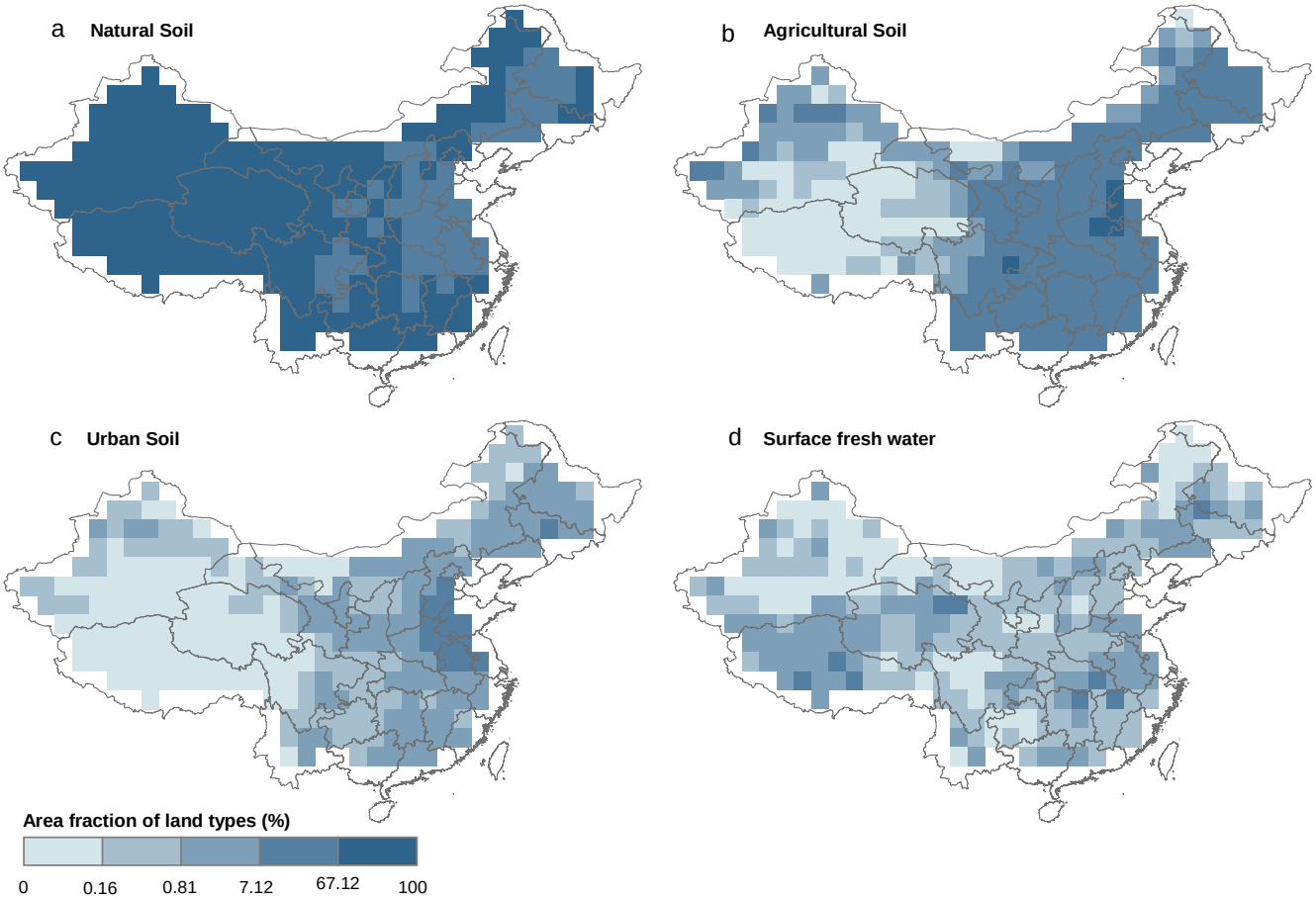

Fig. S8. Area fraction of four land use types for each of 200 × 200 km^2 grids in China

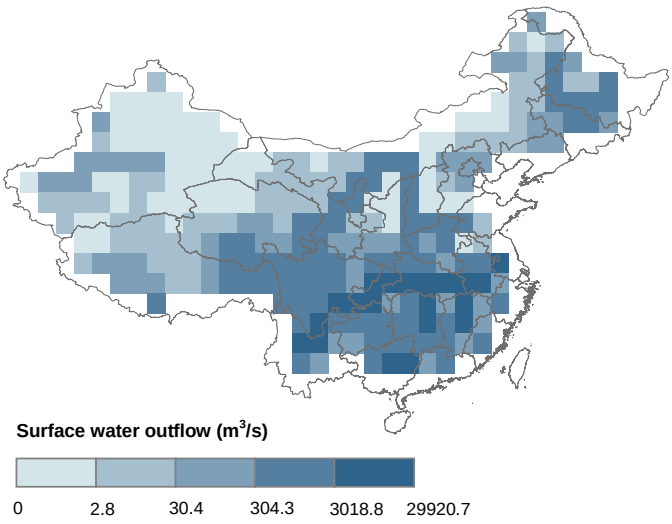

Fig. S9. Surface water outflow for each of 200 × 200 km^2 grids in China

Reference

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II

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Environmental Distributions of Benzo[*a*]pyrene in China: Current and Future Emission Reduction Scenarios Explored Using a Spatially Explicit Multimedia Fate Model

Ying Zhu,[†] Shu Tao,[‡] Oliver R. Price,[§] Huizhong Shen,[‡] Kevin C. Jones,[†] and Andrew J. Sweetman*[,†]

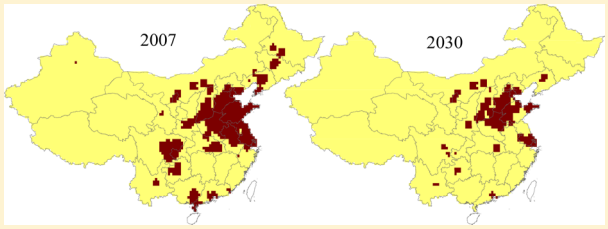
[†]Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, United Kingdom

[‡]Laboratory for Earth Surface Processes, College of Urban and Environmental Sciences, Peking University, Beijing 100871, China

[§]Safety and Environmental Assurance Centre, Unilever, Sharnbrook MK44 1LQ, United Kingdom

Supporting Information

ABSTRACT: SESAMe v3.0, a spatially explicit multimedia fate model with 50 × 50 km^2 resolution, has been developed for China to predict environmental concentrations of benzo[*a*]pyrene (BaP) using an atmospheric emission inventory for 2007. Model predictions are compared with environmental monitoring data obtained from an extensive review of the literature. The model performs well in predicting multimedia concentrations and distributions. Predicted concentrations are compared with guideline values; highest values with some exceedances occur mainly in the North China Plain, Mid Inner Mongolia, and parts of three northeast provinces, Xi'an, Shanghai, and south of Jiangsu province, East Sichuan Basin, middle of Guizhou and Guangzhou. Two potential future scenarios have been assessed using SESAMe v3.0 for 2030 as BaP emission is reduced by (1) technological improvement for coal consumption in energy production and industry sectors in Scenario 1 (Sc1) and (2) technological improvement and control of indoor biomass burning for cooking and indoor space heating and prohibition of open burning of biomass in 2030 in Scenario 2 (Sc2). Sc2 is more efficient in reducing the areas with exceedance of guideline values. Use of SESAMe v3.0 provides insights on future research needs and can inform decision making on options for source reduction.



INTRODUCTION

Inputs of polycyclic aromatic hydrocarbons (PAHs) into the environment are largely derived from inefficient combustion processes, and several are known mutagens/carcinogens.[1−3] They are of environmental and public health concern, so many countries have developed environmental emission and quality criteria. They are also the subject of international agreements and concern due to their long-range atmospheric transport potential.[4−8] While emissions and atmospheric concentrations have been declining in some developed countries,[9−13] global emissions inventories show shifts in primary emissions to rapidly developing countries,[10] where inefficient fossil fuel combustion for power generation, metal production, and other industrial processes, along with transport, waste incineration, and biomass burning, are often major sources.[10] China is now a key part of the global inventory, constituting an estimated 20% of the global emissions in 2007.[10] It is, therefore, particularly important to understand/confirm the key sources in China, where they are distributed, and how efforts at control may affect contemporary and future environmental concentrations.

Benzo[*a*]pyrene (BaP) is a carcinogenic high molecular weight PAH that is emitted to the atmosphere on fine particulates (PM10 and 2.5) and often associated with black carbon (BC). The estimated emission of BaP across China in 2007 was ∼1100 tonnes.[10] However, spatial resolution is important for China, a country of >1.3 billion people, because the population, industrial development, PAH sources, and environmental features vary widely. BaP is one of the most studied compounds in China, with many papers reporting on PAHs in the environment. This makes it an ideal choice as a test chemical when exploring the links between sources and environmental levels with a multimedia environmental fate model. Other studies have previously focused on assessing human exposure to airborne PAHs via inhalation[14−16] and the distribution and ecological risk of waterborne PAHs in seven major river basins by collecting measured data from literature.[17] China has also recently released a National Soil Pollution Gazette reporting on a countrywide soil pollution survey.[18] This survey may result in new legislation that addresses soil protection for China. However, despite there now being (i) specific source inventory information; (ii) a prevalence of air, water, and soil data; (iii) Chinese national standards for BaP in air, water, and soils;[19−21] and (iv) commitments made to

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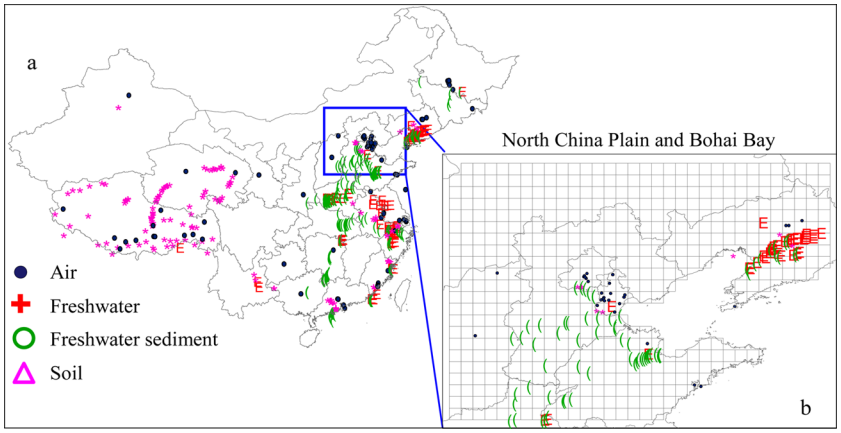

Figure 1. (a) Sampling sites of observed data taken from the literature across China; (b) illustration of the 50 × 50 km^2 grid covering North China Plain and Bohai Bay in the model and the overlay of sampling sites and model grid.

reduce and regulate[22] emissions of particulate matter and other air pollutants by the State Council of China (SCC) 5 year Action Plan for Air Pollution Control,[23] there has been little attempt to integrate this information with multimedia modeling tools or to assess the potential impacts of sources and their controls on ambient levels and, ultimately, for risk management. That is, therefore, the purpose of this article.

Previous multimedia models developed by other researchers have been neither parametrized with fine enough spatial resolution for China[24−26] nor performed on a national scale.[27−30] As a result, we have developed SESAMe v3.0, a spatially explicit multimedia fate model, which has been specifically parametrized for the whole of mainland China with 50 × 50 km^2 resolution. Initially, the model uses spatially resolved BaP atmospheric source inventory information for 2007[10] to generate model predictions to compare with environmental monitoring data obtained from the literature over the period 1997−2011. Quantification of the transfer of BaP between media is briefly discussed in relation to atmospheric transport, key storage media, ambient distributions, etc. On the basis of the good model performance, predicted high background regions are identified across the country by comparing predicted ambient BaP levels with guideline values developed for air, freshwater, and soils. We then move on to explore two possible future scenarios where emission from coal and biomass burning are controlled and reduced by 2030 and to make comparisons with the base year, 2007. This is important, given the opportunity in China for large-scale state intervention and control of sources (e.g., power stations, waste incinerators, vehicles) as well as changing patterns of individual behavior on the consumption of biofuels. SESAMe v3.0 has been used to assess the efficiency of emission reduction in the two scenarios. Our purpose is to show how multimedia models such as SESAMe v3.0 could be used to make informed decisions about possible source control options.

MATERIALS AND METHODS

Model Definition. SESAMe v3.0 is an improved version of the previously described SESAMe model,[31] with equations for transport processes taken from Simplebox 3.24a[32] and MAMI III[33] models; it has a higher spatial resolution than that of SESAMe, with 5468 independent 50 × 50 km^2 grid cells that cover mainland China, and is therefore similar in structure to ChemCan[26] and CHEMFRANCE.[34] Each grid cell represents a region, which is surrounded by eight adjacent 50 × 50 km^2 grid cells that constitute a movable continental scale; the regional scale and the continental scale are connected by nondirectional advective flow exchange, so the model does not directly simulate how BaP is transported from one grid cell to another (for details, see the Supporting Information and Figure S1). This structure, therefore, considers the influence of the emission and environmental processes of the surrounding region to each cell, which is in contrast to ChemCan and CHEMFRANCE. Further improvements have been made for this study, including the addition of seawater compartments, referring to Simplebox 3.24a;[32] spatial data layers for soil density,[35] soil pH,[35] and aerosol contents in air; consideration of the temperature effect on degradation rates, referring to Simplebox 3.24a[32] (Supporting Information); and the inclusion of agricultural soil irrigation by surface freshwater to ensure environmental processes in the model more complete. For agricultural soil irrigation, this version of the model assumes that ∼370 billion m^3 water was consumed in the whole country for irrigation[36] and distributed uniformly to agricultural soil across the country and that the irrigation water in each grid cell originated from local freshwater sources in the same grid cell. Each grid cell has compartments describing air, freshwater and sediment, seawater and sediment, natural soil (defined as forest land, grassland, desert, wetland, and all the other unused land), agricultural soil (cropland soil), urban soil (rural residential land was included), natural vegetation (on natural soil), and agricultural vegetation (on agricultural soil). There are 65 environmental parameters for each grid cell, in which 47 are fixed default values for all regions and 18 are spatially variable (Tables S1 and S2, Supporting Information); the chemical parameters of BaP are given in Table S3.

Emission Inventory. The BaP emission data set for the year 2007 used in this study originated from Shen et al.[10] From their study, it was estimated that the emission of BaP in 2007 for the whole of mainland China (exclusive of Taiwan and Hainan islands) was approximately 1032 tonnes. Nationally, the major BaP sources in China are indoor biomass burning (43%, firewood and crop residue), coke production (21%), and primary Al production (12%); domestic coal burning accounts for about 13%; motor vehicle emissions constituted only an estimated 2%; and open fire agriculture waste burning, 1.2%.[10] However, the dominant sources vary geographically as a complex function of industrial activity, urbanization level, living standards, climate, and policies across China. For example,

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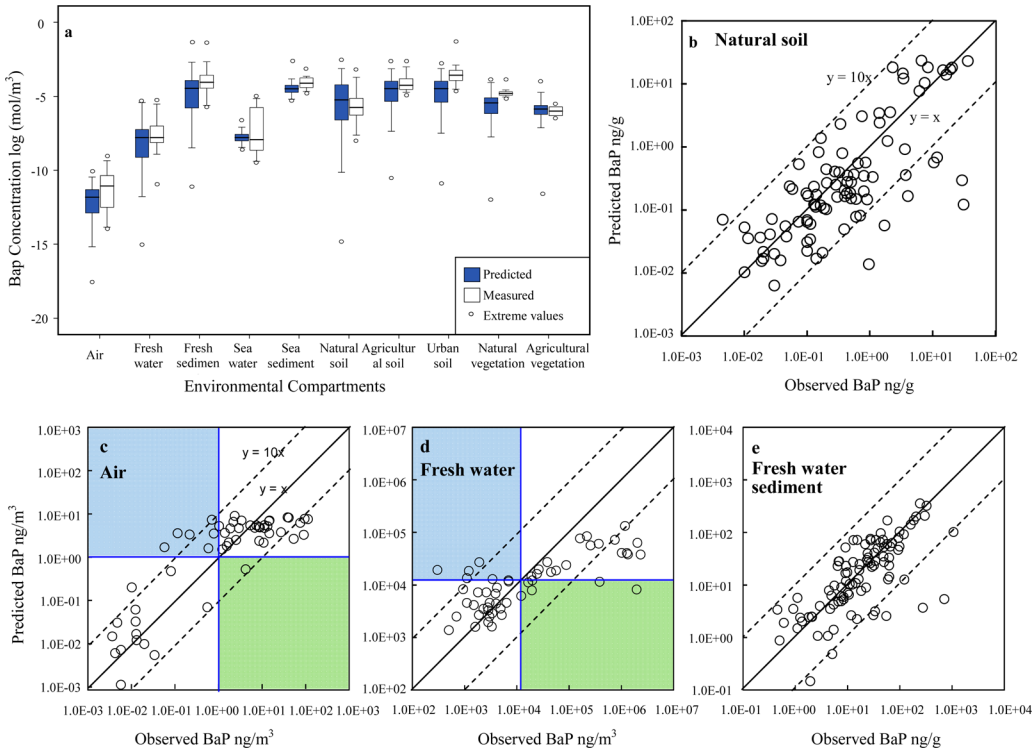

Figure 2. (a) Comparison of predicted (all predicted data) and measured BaP concentrations in each compartment across China; (b–e) point-to-point comparison of BaP concentrations in natural soil, air, freshwater, and sediment (only predicted data with corresponding measured data was used); the blue lines in (c) and (d) are BaP guideline values for air (1 ng/m^3) and freshwater (1.5 × 10^4 ng/m^3).

indoor biomass burning is an important source in large areas of the North China Plain (NCP), Yangtze River Delta (YRD), Anhui, Hubei, Sichuan and the northeast provinces, etc.; coal consumed in coke production is a major source in Shanxi and Inner Mongolia (Ordos); and vehicle diesel is an important source for Shanghai and parts of Beijing.[10] Sources were aggregated in the 50 × 50 km^2 grid, as detailed in the Supporting Information, with the national distribution shown in Figure 4a.

Model Evaluation. Emissions for the base year of 2007 were run to steady state to generate predicted BaP environmental concentrations, which could be compared with measured data and the environmental guideline values/quality standards. The following guideline values were used: ambient air quality values of 1 ng/m^3 as an annual average and 2.5 ng/m^3 as a daily average;[19] soil values of 100 ng/g taken from the Technical Regulations for National Soil Contamination Assessment[37] for Chinese soil pollution survey for soil pollution identification, to compare with the results in the National Soil Pollution Gazette; and freshwater guideline values of 2.8 ng/L from Chinese standards[20] and 15 ng/L from Canadian standards.[38]

To evaluate the model, hundreds of peer-reviewed papers on BaP occurrence in China were found. BaP concentration data were compiled without any filter for environmental media from ca. 130 peer-reviewed literature sources where sampling site location information was given. Focus was given to sampling years 1997–2011 and proximity to the 2007 base emission year (Table S4). Figure 1 shows the location of the measurement data used for air, freshwater, freshwater sediment, and soil. When several sampling sites fall into the same grid cell (Figure 1b), the mean measured value was taken to compare with the predicted concentration in that grid cell.

The dimensions of the selected continental and regional scales within the current model structure are believed to be suitable to capture the majority of the emissions considering the transport distance of BaP is probably a few hundreds of kilometers. However, to ensure that the selected spatial scale is appropriate for BaP, it was compared with two previous versions of the model that have different spatial scales and grid cell dimensions (for more details, see the Supporting Information).

The uncertainty of SESAMe v3.0 was explored by Monte Carlo simulation (for details, see the Supporting Information). The BaP concentration in 10 media was calculated 10 000 times. Normal and log-normal distributions were assessed according to the probability distribution of different input parameters. Values for the emission vector and the 18 environmental variable vectors were randomly produced based on their probability distributions. A variability-based sensitivity coefficient (SCV; see the Supporting Information) was applied to the sensitivity analysis, considering the coefficient of variation of the 18 spatially variable parameters[28] for identifying influential parameters. The parameters with an SCV index > 0.1 were identified as being the most influential to the model output.

MODEL EVALUATION AND DISCUSSION OF RESULTS

This version of SESAMe predicts regional or countrywide background concentrations. Such models do not identify hotspots, but they do predict the regional/grid cell averaged background levels. Figure 2a presents a comparison of predicted and measured BaP concentrations for each modeled environmental compartment. Generally, the agreement across all media is good, with the model capturing the range and actual

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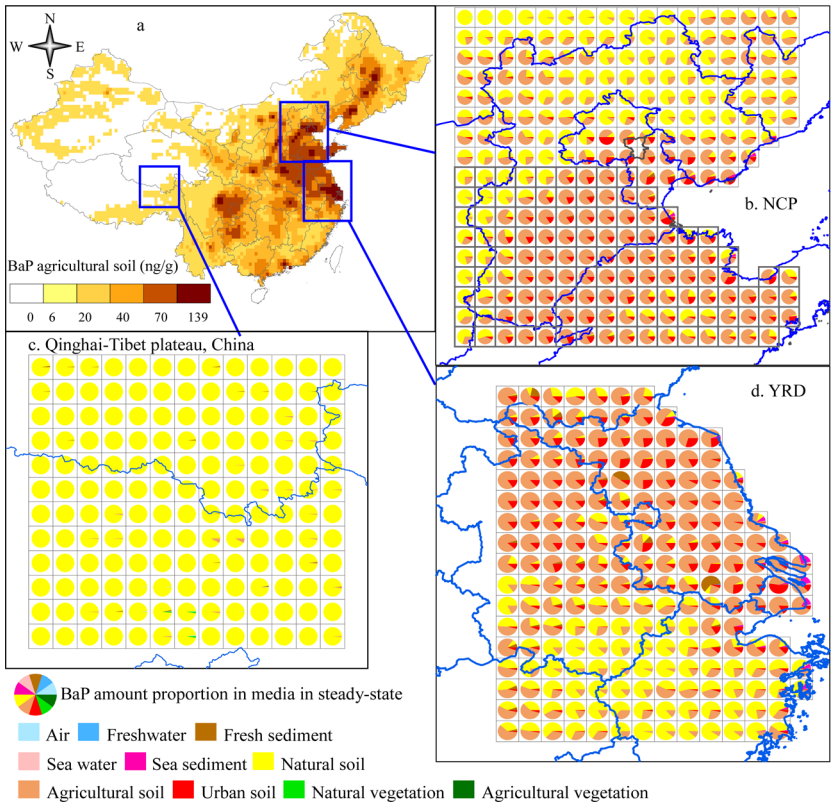

Figure 3. (a) Predicted BaP background levels in agricultural soil; proportional mass of BaP in different environmental media under steady-state in (b) North China Plain (NCP), (c) Qinghai−Tibet plateau, and (d) Yangtze River Delta (YRD).

concentrations very effectively. Most points fall within the 1:10 line, with many clustered around the 1:1 line (Figures 2b−e and S4), which indicates that model performance is better for freshwater, sediment, and soil than that shown by Simplebox 3.0, EVn-BETR, and IMPACT2002 in the study by Armitage et al.[39] The selected dimensions of the regional and continental scales are important for models of this type. The selected grid dimensions in SESAMe v3.0 provide improved agreement with the measurement data compared to that from two previous versions of the model with different grid dimensions for regional and continental scales (Supporting Information). Figure 2a suggests that a small systematic underprediction appears for several media but not for background concentrations. Often, the measured data collected from the literature highlights industrial parks or cities,[40,41] agricultural soil irrigated by wastewater,[42−44] locations where dense coal burning for heating takes place,[45] urban areas with intensive transportation,[46−48] and so on, e.g., those points falling below the lower 1:10 line. This may cause the underestimation shown in Figure 2a, but the model actually reflects the average situation in each grid cell. As precipitation is assumed to be continuous in the model, it is most likely to overestimate deposition rates for BaP,[49] leading to the underestimation of air concentrations in some regions. However, this effect appears to be limited on a national scale. The distribution of BaP concentrations in different media is log-normal, and the interquartile range can be found in Supporting Information Figure S3 obtained from the Monte Carlo simulation.

BaP Transport and Partitioning between Media. The model predicts that after being released to the atmosphere BaP is mainly transported to soils, water, and vegetation by wet and dry deposition of particle-bound BaP; from water to sediment by sedimentation and absorption; from vegetation to soils by litter production; and from soils to water by runoff (see Figures S5 and S6). The reverse processes, volatilization to air, desorption and resuspension from sediments, and transpiration, are relatively unimportant. Higher precipitation rates increase the particle-bound BaP flux scavenged from air to soil or water. Areas with high soil organic matter (e.g., northeast in Heilongjiang Province) will have greater storage and retention of BaP. BaP reaches above ground vegetation primarily via particle-bound deposition rather than from soils, in agreement with measured and other modeling studies.[43,50,51]

Soil is the primary sink for BaP in China; at steady state, 99% of BaP will be found in soil. The model defines different soil land use categories, so nationally the loadings are ∼56% in agricultural soils, 35% in natural soils, and 8% in urban soils. Obviously, there are major regional differences, for example, with most BaP found in natural soils in the Qinghai−Tibet plateau, in agricultural soils in NCP and Jiangsu, and urban soils in Shanghai (Figure 3). For some coastal or inland catchment regions, most BaP is found in sediments (Figure 3d). Storage in sediments is significant only for the mass balance in the coastal or freshwater catchment regions. The SCV index in Table S5 shows that the BaP concentration in a region can be affected by the emission and some environmental parameters in surrounding regions. Some grid cells are more influenced by emission and environmental processes at the surrounding continental scale than those within its own cell.

Spatial Distribution of BaP. The model predicts a range of regional background concentrations (5th−95th percentiles, plus median) in the different media as follows: air, 0.002−4.6 ng/m^3 (median, 0.4 ng/m^3); soils, 0.002−51 ng/g for natural soil (0.9 ng/g) and 0.05/0.06−56/58 ng/g for agricultural/

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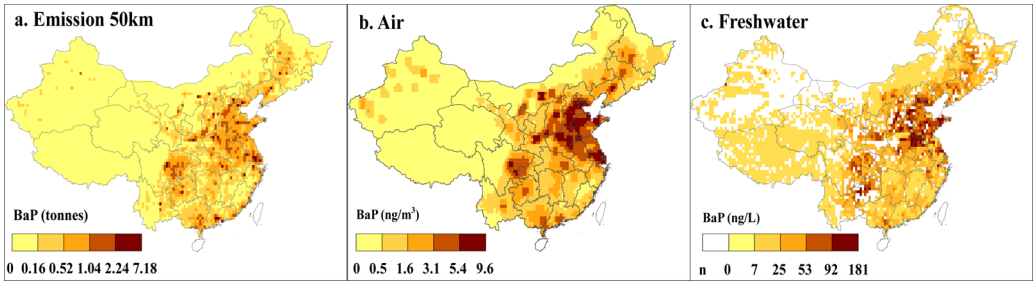

Figure 4. (a) BaP emission;[10] predicted BaP backgrounds levels in air (b) and freshwater (c); in (c), n = no freshwater.

urban soil (6.4 ng/g); fresh and seawater, 0.002−60 (4) ng/L and 1.5−11 (3.5) ng/L; fresh and marine sediments, 0.004−96 ng/g (6 ng/g) and 1.7−17 ng/g (5 ng/g); and vegetation, 0.0003−4 ng/g (0.1 ng/g) and 0.001−1.8 ng/g (0.2 ng/g) in natural and agricultural vegetation (Figures 3, 4, S7, and S8).

The predicted geographic distribution pattern is generally similar for air, soils, and vegetation and the emission distribution pattern on the national scale (Figures 3 and 4). Air, soil, and vegetation concentrations are generally predicted to be higher in areas such as NCP, Mid Inner Mongolia (Baotou, Ordos, and Hohhot), part of the three northeast provinces (middle of Liaoning and Jilin provinces and south Heilongjiang), Xi'an in Shaanxi province, Shanghai and south of Jiangsu province, East Sichuan Basin, middle of Guizhou, Guangzhou in Guangdong province. However, environmental conditions can produce contrasting regional air and soil backgrounds. For example, a region in south Hebei has the same air concentration but nearly three times the concentration of BaP in soil compared to that in a region in west Inner Mongolia (Baotou). As the emission in the region of south Hebei is much higher and with higher precipitation rates in NCP compared to that in Inner Mongolia, more BaP is transferred to soils after being released to the atmosphere. Another interesting contrasting region in Liaoning in northeast China exhibits high soil levels close to that in another region in north Tianjin, but the air concentration is only half of that in the region in Tianjin. Runoff is similar in the two regions, but the higher soil OC contents in Liaoning enhance BaP retention by soil. For most of these areas, the high background concentrations are caused mainly by indoor biomass burning (crop residue and firewood); in contrast, in Inner Mongolia, middle of Guizhou, Xi'an, some areas in Shanxi, Hebei, and Shandong province in NCP, coal consumed by industry is also a key source.

Primarily, BaP emissions reach aquatic systems via deposition and soil runoff. The geographic distribution in freshwater and sediment viewed on the country scale is similar to that in air and soil. However, regional differences are apparent, caused by variation in the discharge volume of rivers, runoff, soil OC, etc. For example, BaP concentrations are extremely low in Shanghai, south Jiangsu province (22 ng/L in freshwater; 35 ng/g in sediment) in the lower reaches of the Yangtze River, and the lower reaches of Yellow River (20 ng/L in freshwater; 31 ng/g in sediment) in NCP, but the air and soil concentrations in the two regions are relatively high. A region with predicted high water concentrations (173 ng/L) in the northern boundary of Anhui province has a moderate predicted BaP level in soil (68 ng/g) because the soil OC contents are lower here and runoff can transfer more BaP from soil to water, but the water discharge volume is also low.

Large areas in western China (e.g., Qinghai−Tibet plateau, large areas of Xinjiang) have lower predicted median BaP values. They are generally of the order of 0.04 ng/m^3 in air, 0.06 ng/g in natural soil, 0.32 ng/g in agricultural and urban soil, 0.06 ng/L in freshwater, 0.1 ng/g in sediment, and ca. 0.006 ng/g in natural and agricultural vegetation.

Comparison of Regional Values and Suggested Guideline Values for Different Media. The previous sections show that the model performs well in predicting environmental concentrations. Air, soil, and freshwater are important media for public health and, as noted earlier, have guideline values suggested in China and elsewhere. For air, 2.5 ng/m^3 has been proposed as a daily average standard. The model predicts that this is exceeded in ca. 13% of mainland China (e.g., NCP, three northeast provinces, Shanxi, north Ningxia, mid Inner Mongolia, YRD, east Sichuan, mid Guizhou, Pearl River Delta (PRD), southeast Guangxi, etc.). A value of 1 ng/m^3 has been proposed as an annual average. This is exceeded in ca. 32% areas of mainland China (e.g., additional areas such as north and west of Guangxi, south Ningxia, south Gansu, Hunan, and coastal areas in Fujian province). This exceedance ratio is close to 30% obtained in another Chinese study using the model CanMETOP, which used a 1 km^2 spatial resolution.[14] For soils, 100 ng/g has been adopted as a guideline value for all soils in Technical Regulations for National Soil Contamination Assessment[37] for the national soil pollution survey. This is predicted to be exceeded in ca. 0.25% of soils in mainland China. In contrast, this is exceeded by 1.4% of the sampling sites across China in the National Soil Pollution Gazette,[18] which reports the result of national soil pollution survey, probably because it is indicated in the Gazette that many samples were taken from seriously contaminated land. 100 ng/g is also proposed as the Chinese soil quality standard value for agricultural soil. The model predicts that it is exceeded by ca. 0.8% (about 22 000 km^2) for agricultural soil. These regions are mainly in Shanghai, south Jiangsu, Tianjin, and Liaoning (Shenyang and Liaoyang). For freshwater, 15 ng/L has been proposed as the Canadian guideline value. It is exceeded by ca. 13% (ca. 20 000 km^2) of freshwater in mainland China (e.g., NCP, northeast China provinces, Shaanxi, Guizhou, and east Sichuan). A value of 2.8 ng/L is proposed as the Chinese standard value. It is exceeded in ca. 40% (ca. 69 000 km^2) of freshwater (covering almost half mainland China in the east). The overestimation of median or low concentrations (blue area in Figure 2c,d) and the underestimation of high concentrations (green area in Figure 2c,d) may cause a small but acceptable bias of exceedance rates estimation but demonstrates good performance of the model.

Future Scenario Selection. In this section, we illustrate how the model can be used to investigate the efficiency of source reduction/controls. Two scenarios are used to generate

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possible future ambient concentrations for the nominal year 2030.

The State Council of China (SCC) has made a 5 year Action Plan for Air Pollution Control.[23] This refers to controlling current major industrial emissions (e.g., by improved combustion and stack controls); reducing the usage of and dependence on coal, particularly in the Beijing−Tianjin−Hebei region, the Yangtze River Delta, and the Pearl River Delta; expediting the use of clean energy; controlling the number of vehicles or encouraging electric vehicles; and so on. Control measures that could be most relevant to BaP emissions relate to the use of coal in industry and energy production.

Future Scenario 1 (Sc1). This considers control of coal consumption in two sectors (centralized energy production and major industrial sources). The following assumptions and principles were used to develop this scenario:

(1) Coal consumption itself was not changed (2007 and 2030 levels were assumed to be the same), as it is unrealistic to foresee a reduction in coal usage in 2030 considering that the coal consumption/production in China has risen by ca. 48% from 2007 to 2012,[52] and may currently be higher, with many researchers arguing that coal consumption is likely to remain high and key to China's economic growth.[53−56] However, an action plan was developed in 2013 to reduce the coal usage in certain regions, and the percentage of coal consumption in total energy consumption in China declined ca. 6% from 2007 to 2012;[57]

(2) The emissions from key sources were assumed to be reduced between 2007 and 2030 by improvements in technology and combustion conditions (see Table 1 for details);

Table 1. Percent Usage of Different Technologies in Each Sector (EFs mg/tonnes[a,10])

coal	sectors	energy production		industry	
(Sc1)	technology	no control	control	no control	control
	2007	30% (1.2)	70% (1.4×10^{-2})	53% (40)	47% (0.46)
	2030	1.8% (1.2)	98.2% (1.4×10^{-2})	12.5% (40)	87.5% (0.46)
biomass	activities	indoor crop residue burning		indoor firewood burning	
(Sc2)	technology	traditional stove	improved stove	traditional woodstove	improved woodstove
	2007	66% (1.8)	34% (0.69)	63% (1.5)	37% (0.56)
	2030	16% (1.8)	84% (0.69)	15% (1.5)	85% (0.56)

[a]The unit of EFs, mg/tonnes, means the amount of BaP (mg) released by burning one tonnes of coal or biomass.

(3) The fraction of uncontrolled and controlled activities was calculated by assuming improved technologies are introduced as described by Bond et al.[58] in their projections about future black carbon emission scenarios. Controlled coal boilers were assumed to increase from 70 to 98% for energy production and from 46 to 87% for industry (see Supporting Information for further details and Table 1);

(4) Emission factors (EFs) were assumed stable over time for uncontrolled sources, whereas improved EFs were employed for the controlled sources. These were derived from Shen et al.,[10] with average values from their report being given in Table 1;

(5) The technology improvement in the energy and industry sectors was presumed to be performed in the regions of China where coal consumption in the two sectors was >50% to all sources or in the regions with air backgrounds > 1 ng/m^3.

Future Scenario 2 (Sc2). This scenario considered indoor domestic burning for cooking and heating homes/buildings. Crop residues and firewood are important sources in some parts of China, especially in areas with higher predicted background concentrations in this study,[10,59] and, while this can be an important source of indoor air pollution and associated human health concerns,[60,61] here we focus on the potential contributions to ambient air. The following assumptions were made:

(1) A fraction of traditional and improved combustion stoves was calculated by assuming improved technologies are introduced as described by Bond et al.[58] The percentage of improved stoves was assumed to increase from 34 to 84% for indoor crop residue burning and from 37 to 85% for indoor firewood burning (see Table 1);

(2) EFs were assumed stable over time for the individual technology as shown in Table 1, and the average values reported in Shen et al.'s research[10] were adopted;

(3) BaP EFs were assumed to be reduced by 40% when improved stoves are used for indoor crop residue burning and indoor firewood burning (Table 1). At the same time, half of the indoor crop residue and indoor firewood burning activities were assumed to be reduced due to urbanization or other alternatives (e.g., induction cookers) introduced to rural residents for cooking and heating. It has been projected that half of the rural areas in 2007 could become urbanized before 2030, which is based on the urbanization rate of China in the past 10 years (1% each year conservatively), as reported by the World Bank,[62] and an assumption that this rate is maintained until 2030 in regions described in (4) below. Indoor biomass burning is banned in urban areas in China;

(4) The technology improvement and biomass burning reduction by urbanization or the other alternatives were performed in the regions of China where the indoor biomass (crop residue and firewood) burning was >50% to all sources or in the regions with air backgrounds > 1 ng/m^3;

(5) Open fire burning of agricultural waste is prohibited or regulated in many countries or regions.[63−65] China also has released a draft version of the Law of People"s Republic China on the Prevention and Control of Air Pollution in which open burning of biomass in densely inhabited districts, areas near airports, or the main traffic ways should be forbidden.[66] All open burning of agricultural waste was assumed to be successfully banned by 2030.

Outcomes Predicted by the Future Scenarios. By adopting improved technology and EFs in Sc1, BaP emissions would decline by 90 and 75% by 2030 in the energy production and industry sectors, respectively, from coal consumption in selected regions in Sc1. The total annual emission would decrease to ca. 900 tonnes/year in mainland China. By

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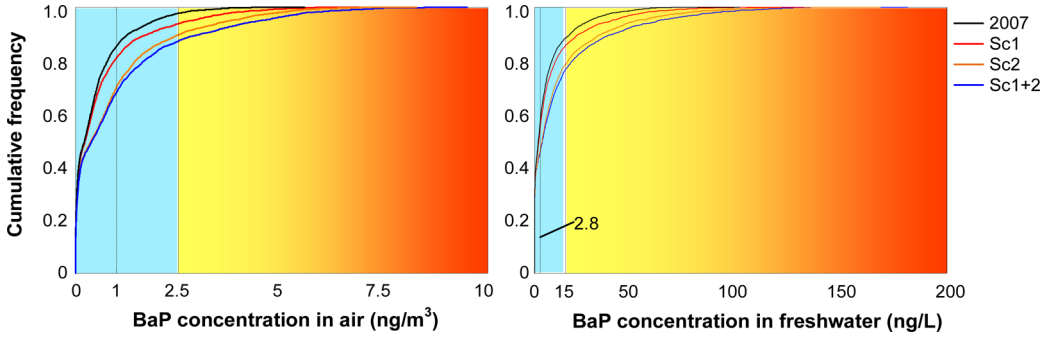

Figure 5. Cumulative frequency of BaP concentration in air (left) and in freshwater (right).

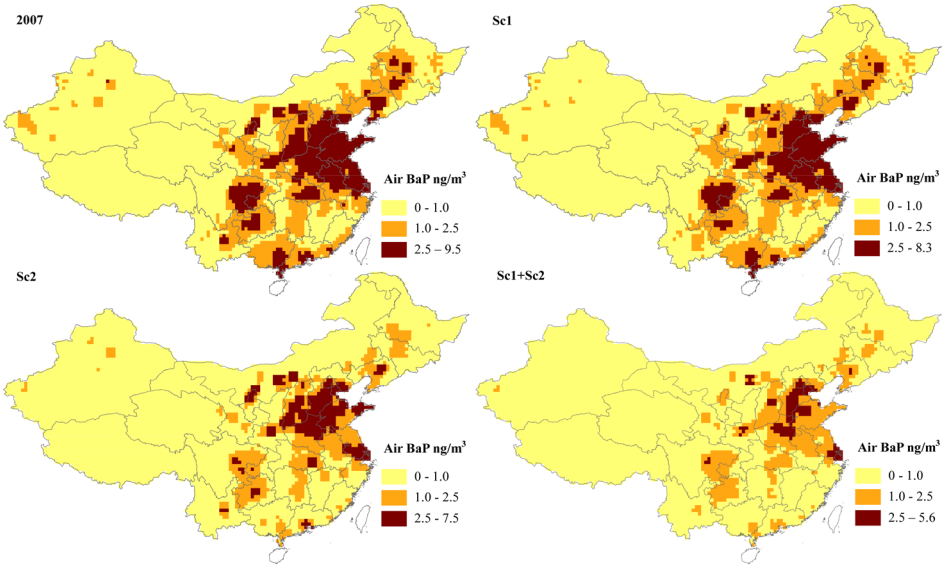

Figure 6. BaP air concentration in 2007, Sc1, Sc2, and Sc1 + Sc2.

adopting improved stoves and EFs and the assumed urbanization scenario in Sc2, BaP emission would decline by 70% from indoor crop residue and firewood burning by 2030 in selected regions in Sc2. The total annual emission would decrease to ca. 610 tonnes/yr in mainland China. Since the two scenarios do not conflict, if implementing Sc1 + Sc2, then the total annual emission would decrease to ca. 470 tonnes/year in mainland China.

Figures 5 and 6 show how more efficient Sc2 is than Sc1 in reducing the regional levels of BaP in air and freshwater. The areas where regional background concentrations would exceed 2.5 and 1 ng/m^3 in air are reduced by ca. 19 and 6%, respectively, in Sc1 and ca. 51 and 40% in Sc2. Technology improvement for coal consumption is efficient in reducing backgrounds to <2.5 ng/m^3 only in areas such as Shanxi and boundary of north Ningxia and Inner Mongolia where there are coal mines (Figure 6). Implementation of the biomass burning and consumption control in Sc2 would reduce the regional concentration to <2.5 ng/m^3 in the northeast provinces, NCP, Jiangsu, Anhui, Sichuan, and Guangxi. Indeed, it would reduce BaP levels in large areas in these regions below the 1 ng/m^3 annual guideline value.

For freshwater (Figure S9), the areas where regional backgrounds would exceed 2.8 ng/L are reduced by ca. 20% in Sc2 but show almost no reduction in Sc1, and those that would exceed 15 ng/L are reduced by ca. 20 and 50%, respectively, in Sc1 and Sc2. Technology improvement on coal consumption in Sc1 would have little effect in reducing freshwater backgrounds to <2.8 ng/L but would work in small regions in north Ningxia, Gansu, and Yunnan in reducing the background concentration to <15 ng/L. Implementation of Sc2 would be efficient in reducing the background level to <15 ng/L in northeast China, east Sichuan, south Henan, and Hubei, and it is efficient in southeast China in reducing backgrounds to <2.8 ng/L.

The current commitments in government regulations and action plans for air pollution prevention and control focus mainly on reducing coal usage or improving technology on coal consumption. These scenarios suggest that if greater efforts were put into biomass burning control and technology improvement at the same time, as shown in Figures 5 and 6 (Sc1 + Sc2), the areas with air background exceedance of 2.5 and 1 ng/m^3 could be reduced by 82 and 54%, respectively, and for freshwater background exceedance of 2.8 and 15 ng/L, it could be reduced by 34 and 65%. It is also necessary to reduce emissions to both the regional grid cell and to its surrounding area for effective pollution control considering the emission and input from surrounding areas will also influence regional contamination (Figure S10).

This section provides an illustration of the model application in the future scenario discussions above. SESAMe v3.0 can perform well on assessing the efficiency of potential implementation of policy made by governments or scientific research on preventing or controlling pollution nationally or

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regionally. We stress that the scenarios are hypothetical and make no claim about their likely development in the future.

Potential Future Applications for SESAMe v3.0 as a Pollution Management Tool. In reality, future Chinese emission scenarios will be determined by a complex combination of driving forces such as socio-economic development, large-scale state intervention, technology development, climate change, and so on. They are evolving dynamically with high uncertainty, so no realistic future scenarios can be predicted confidently.[67] However, research into possible scenarios can provide useful information to support decision/policy makers to prepare for the challenge of reducing environmental pollution in the future.

It has been demonstrated in this study that utilizing models such as SESAMe v3.0 for both current and future scenario evaluation could provide valuable information for decision making on emission reduction strategies and pollution management. Assessment of current multimedia BaP concentrations across China assists in the identification of which regions would be most affected by the implementation of the two considered scenarios. Major emission sources were also considered when selecting regions for study. It can, therefore, be considered an economical way to evaluate the potential of commitments for pollution control in selected regions rather than in the whole country. Multimedia models have been selected for risk evaluation or pollution management and decision making by a wide range of researchers and government institutions.[68−71] SESAMe v3.0, as a multimedia model, has the advantage of supporting science and decision making for the evaluation of future pollution reduction and management.

■ ASSOCIATED CONTENT

Supporting Information

Additional information on description of methods, input model parameters, the literature for collecting measured data, and the output figures. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b00474.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: a.sweetman@lancaster.ac.uk; Tel: +44 1524 594715 and +44 1524 595994.

Notes

The authors declare no competing financial interest.

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Supporting Information for

Environmental Distributions of Benzo[a]pyrene in China: Current and Future Emission Reduction Scenarios Explored Using a Spatially Explicit Multimedia Fate Model

Ying Zhu[1], Shu Tao[2], Oliver R. Price[3], Huizhong Shen[2], Kevin C. Jones[1], and Andrew J. Sweetman[1]*

[1]Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, United Kingdom

[2]Laboratory for Earth Surface Processes, College of Urban and Environmental Sciences, Peking University, Beijing 100871, China

[3]Safety and Environmental Assurance Centre, Unilever, Sharnbrook MK44 1LQ, United Kingdom

*Corresponding author E-mail: a.sweetman@lancaster.ac.uk; Tel: +44 1524 594715 and +44 1524 595994

29 pages; 6 tables; 10 figures; 8 equations

Table list

Figure list

Model definition

SESAMe v3.0 used in this study was improved from an earlier version SESAMe[1]. The resolution was improved to 50 × 50 km^2. The boundary grid cells with land area fraction within China >50% were included. As shown in Figure S1, the continental scale comprises 8 surrounding grid cells within which it is assumed to be homogeneous. The average value of the individual environmental parameter and the sum of the emission for the eight surrounding grid cells were taken as the input of the continental scale. When the regional grid cell moves, the continental scale moves together (e.g. from region 1 to 2 in Figure S1). For the boundary grid cell, the eight closest surrounding 50km grid cells comprise the continental scale. This is different from SESAMe. In SESAMe the continental scale is fixed and represents the whole of mainland China outside each of the 200 × 200 km^2 grid cells. This is similar to the structure of the Simplebox model. The mass exchange between the regional and the continental scale is represented by the advective transport flow for the air and water compartments. This structure enables an input concentration in advective inflow for each regional grid cell (the central cell). However the model doesn't directly simulate the directional transport of BaP from one grid cell to another. The output of each of the 5468 independent 50km grid cells are predicted independently.

The 18 environmental variables, 47 fixed default environmental parameters and physico-chemical parameters of BaP are in Table S1-S3.

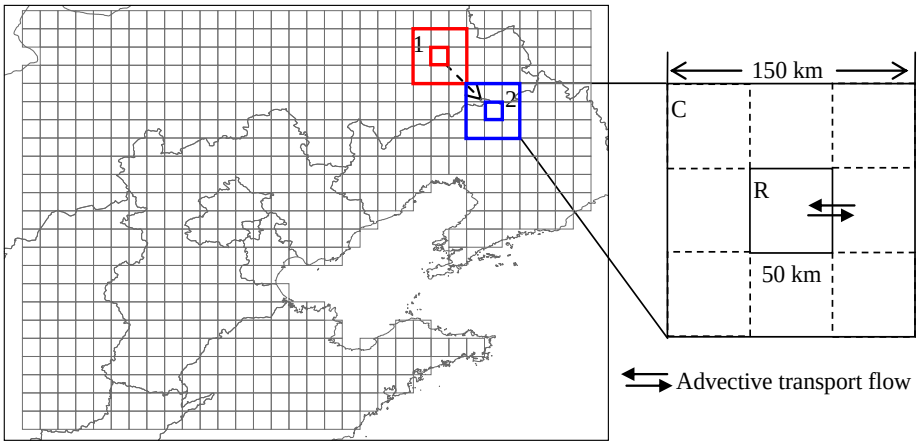

Figure S1. The structure of the SESAMe v3.0 model. The expanded area covers the North Plain China (NPC) and Bohai Bay as an example. C, continental scale; R, regional scale. The continental scale moves with regional scale together from 1 to 2 and as it is across the country

Table S1. 18 environmental variables for 50×50 km^2 grid representing mainland China

No.	Variables	Unit	Range	Median*
1	Area fraction of nature soil [b]	-[a]	0 – 1	0.92
2	Area fraction of agriculture soil [b]	-	0 – 0.98	0.06
3	Area fraction of urban soil [b]	-	0 – 0.49	1.5×10^{-3}
4	Area fraction of fresh water [b]	-	0 – 0.76	1.3×10^{-3}
5	Area fraction of sea water	-	0 – 0.86	0
6	Area fraction of nature vegetation [c]	-	0 – 0.84	0.035
7	Temperature [d]	K	262 - 297	279
8	Wind speed [e]	m/s	0.77 - 7.7	2.5
9	Precipitation [d] (continuous)	m/s	4.8×10^{-10} - 7.1×10^{-8}	1.4×10^{-8}
10	Surface water depth [f,g]	m	0 - 51	1
11	Fraction of runoff [h]	-	0.15 - 0.49	0.27
12	Soil water erosion rate [i]	m/s	0 - 8.9×10^{-11}	3.9×10^{-12}
13	Fraction of soil organic carbon [h]	-	7.9×10^{-5} - 0.52	0.03
14	Surface water inflow [f]	m^3/s	0 - 2.9×10^{4}	1
15	Surface water outflow [f]	m^3/s	0 - 2.91×10^{4}	3
16	Soil density [h]	kg/L	1.1 - 1.5	1.4
17	Soil pH [h]	-	4.8 - 8.5	6.5
18	Volume fraction of aerosol in air [j]	-	1.0×10^{-13} - 2.5×10^{-9}	4.5×10^{-12}

a -: Dimensionless
b: http://www.geodata.cn
c: http://www.iscgm.org
d:Hijmans et al., 2005 [2]. http://www.worldclim.org. It's global long-term average dataset covering 1950-2000.
e: http://www7.ncdc.noaa.gov, the interpolation method was used to generate the map by using the long-term average gauging values from the website.
f: The surface water inflow, outflow and depth were from or calculated based on the surface water discharge map from Mick J. Whelan [3, 4].
g: The surface water depth was calculated from the surface water discharge [5, 6].
h: http://webarchive.iiasa.ac.at/Research/LUC/External-World-soil-database/
i: It was from the research of Doetterl et al. [7]
j: It was calculated by interpolating the PM10 contents in Beijing [8] to the country scale based on China populatin in 2010 (http://www.ornl.gov/sci/landscan/)
* It is the media value of the raw data for each parameter without transformation.

For the volume fraction of aerosol in air in Table S1, it is difficult to find available spatial distribution data for aerosol concentrations in the air across China. As a result an approximation was made by assuming the aerosol concentrations in the air per capita are the same across the country. A value of 165 ug/m^3 for PM10 concentration in Beijing was reported in the study by Zhou et al. (2005).[8] This value was divided by the population of Beijing to calculate the aerosol concentration in air per capita. The population in each 50km squared grid cell was then extracted from the China population 2010 map (http://www.ornl.gov/sci/landscan/) by using ArcGIS. Combining these information, the PM10 contents in each 50km grid cell was calculated. This approach provided estimated spatial aerosol concentrations in air across China which improved model performance which originally used a fixed value across the country. However, it is acknowleded that measured aerosol concentration data would improve this aspect of the model.

Table S2. The default environmental parameters in model

Environmental compartments	Variables	Unit	Value
Atmosphere	depth	m	1000
	Volume fraction of air	-	1
	Volume fraction of aerosol water	-	2E-11
	Fraction of organic carbon in aerosol	-	0.1
	Aerosol solids density	kg/L	2
	Aerosol solids pH	-	3
	Aerosol water pH	-	3
Soils (natural, urban and agricultural soils)	Depth	m	0.05
	Volume fraction of air	-	0.2
	Volume fraction of water	-	0.2
	Volume fraction of solids	-	0.6
Freshwater	Volume fraction of suspended particles	-	1.15E-05
	Fraction of organic carbon in suspended particles	-	0.05
	pH	-	7.5
Freshwater sediment	Depth	m	0.03
	Volume fraction of water	-	0.8
	Volume fraction of solids	-	0.2
	pH of sediment water	-	7.5
Sea water	Depth	m	10
	Volume of suspended particles	-	2.0E-06
	Fraction of organic carbon in suspended particles	-	0.1
	pH	-	8
Seawater sediment	Depth	m	0.03
	Volume fraction of water	-	0.8
	Volume fraction of solids	-	0.2
	Fraction of organic carbon	-	0.05
	pH of sediment water	-	8
Vegetation	Volume fraction of water (natural and agricultural)	-	0.95
	Volume fraction of dry matter (natural and agricultural)	-	0.05
	Fraction of lipid for natural vegetation	-	0.015
	Fraction of lipid for agricultural vegetation	-	0.012
	Density (natural and agricultural)	kg/L	0.83
	pH of vegetation water (natural and agricultural)	-	5.8
	pH in dry matter (natural and agricultural)	-	7.3
	Leaf area index of natural vegetation	-	3.9
	Leaf area index of agricultural vegetation	-	2.7
	vegetation mass of natural vegetation	kg/m^2	1.2
	vegetation mass of agricultural vegetation	kg/m^2	1.8

Notes: the parameters were taken from Simplebox v3.24a[9] and MAMI III[10].

Table S3. Physico-chemical parameters of BaP

	Variables	Unit	Value
Physical-chemical properties	Molecular Mass	g/mol	252.3
	Vapor pressure at 25 °C	Pa	7.0E-07[11]
	Water Solubility at 25 °C	mol/m^3	1.5E-05[11]
	$K_{OW,neutural}$	-	1.1E+06[11]
	Enthalpy of vaporization	J·mol^{-1}	7.4E+04[a]
	Enthalpy of dissolution	J·mol^{-1}	1.0E+04[9]
	Universal gas constant	Pa·m^3/(mol·K)	8.314
Degradation rates at 25 °C	Atmosphere	s^{-1}	1.1E-06[12]
	Water	s^{-1}	6.2E-07[13]
	Sediment	s^{-1}	5.5E-09[14]
	Soil	s^{-1}	1.2E-08[15]
	Vegetation	s^{-1}	2.0E-07[b]

Notes: a, Enthalpy of vaporization values were collected for around 50 organic chemicals in the chemical database of Simplebox v3.24a[9]. The quantitative correlation of these values and the chemical molecular weights was determined. The enthalpy of vaporization of BaP was predicted by using the correlation with molecular weight. However, this parameter was found not to be very sensitive.
b, $k_{deg\_vegetation25°C} = k_{deg\_soil25°C} \times 17$.

The degradation rates are temperature dependent in SESAMe v3.0. This is also an improvement compared to SESAMe. However, it is not currently possible to consider all factors that may affect chemical degradation rates in the environment.

The temperature dependent degradation rates in different media are calculated as below[9]:

$$k_{deg\_air} = k_{deg\_air25°C} \times F_{temp\_air} \times f_{gas} \quad (1)$$

$$k_{deg\_water} = k_{deg\_water25°C} \times F_{temp\_wsds} \times f_{water} \quad (2)$$

$$k_{deg\_sediment} = k_{deg\_sediment25°C} \times F_{temp\_wsds} \quad (3)$$

$$k_{deg\_soil} = k_{deg\_soil25°C} \times F_{temp\_wsds} \quad (4)$$

$$F_{temp\_air} = exp((Ea.OHrad/8.314) \times (temperature - 298)/298^2) \quad (5)$$

$$F_{temp\_wsds} = Q.10^{((temperature-298)/10)} \quad (6)$$

where F_{temp_air} is the temperature correction reaction rate for air; F_{temp_wsds} is the temperature correction reaction rate for water, sediments and soils; f_{gas} is the fraction of the chemical in gas phase in air; f_{water} is the fraction of the chemical in water phase either in surface freshwater or in sea water; $Ea.OHrad$ is the activation energy OH radical reaction (6000 J/mol in this study); and $Q.10$ is the rate increase factor per 10 °C (2 in this study).

Emission inventory

The original emission inventory of 2007 from research by Shen et al.[16] was 0.1°×0.1° -resolution. It was aggregated to 50 × 50 km^2 resolution for this study by using the 'zonal statistics tool' in ArcGIS 10.2.2 to calculate the sum of emission in each 50 km grid cell.

Model evaluation methods

The ~130 peer-reviewed papers where the measured BaP concentrations and the sampling sites location information were taken are listed in Table S4.

To evaluate if the selected dimensions of the regional and continental grids in SESAMe v3.0 are appropriate for BaP, SESAMe and a version of SESAMe v2.0 (not published) have been compared with SESAMe v3.0. SESAMe has been introduced above; and SESAMe v2.0 is a version with a structure similar to SESAMe v3.0, which has 200 km squared regional scale and 600 km squared (8 surrounding grid cells) continental scale.

The probability distribution of input emission and environmental variables is shown in Figure S1. They are normal or lognormal distribution. Values for the emission and 18 environmental variable vectors were randomly generated according to their probability distribution.

A variability-based sensitivity coefficient (SCV) was adopted to do the sensitivity analysis described in below equation.[17]

$$\mathrm{SCV} = \frac{\Delta CV_i^Y / CV_i^Y}{\Delta CV_i^X / CV_i^X} \quad (7)$$

where CV_i^X and CV_i^Y are respectively the coefficient of variance (CV) of values of the i^{th} input variable vector and the corresponding i^{th} predicted output. ΔCV_i^X and ΔCV_i^Y are the difference of these CV.

Table S4. Sampling location, time, and references of measured BaP occurrence data from the literature

Media	Location	Sampling year	Reference
Air	Shenyang	2001	Tang N, 2005[18]
	Nanjing	2001-2002	Wang G, 2006[19]
	Guangzhou	2001-2002	Li J, 2006[20]
	Tianjin	2002	Wu S, 2004[21]
	Shanghai	2003-2004	Guo H, 2004[22]
	Waliguan, Qingdao	2005	Cheng H, 2006[23]
	Beijing	2005-2006	Zhang S, 2009[24]
	Shanghai	2005-2006	Chen Y, 2011[25]
	Xi'an	2005-2007	Okuda T, 2010[26]

	Beijing	2006	Li Y, 2013[27]
	Guangzhou	2006	Gao B, 2011[28]
	Shenzhen	2006	Liu G, 2010[29]
	Hangzhou	2006-2007	Lu H, 2011[30]
	Tibetan Plateau	2007	Wang C, 2014[31]
	Harbin	2007-2008	Ma W, 2011[32]
	North China Plain	2007-2008	Wang W, 2011[33]
	Changsha	2008	Yang F, 2010[34]
	Lhasa	2008-2009	Ma W, 2013[35]
	Beijing	2008-2009	Ma W, 2011[36]
	Harbin	2008-2009	Wan L, 2010[37]
	Xiamen	2008-2009	Zhao J, 2010[38]
	Beijing	2008-2009	Wu Y, 2014[39]
	Xiaomai	2008-2009	Wang Z, 2013[40]
	Northeast China	2008-2009	Li W, 2011[41]
	Yanbian	2008-2010	Jin G, 2012[42]
	Jiangsu	2009-2010	Zhang L, 2013[43]
	Taiyuan	2009-2010	Xia Z, 2013[44]
	Shenyang, Shanghai, Fuzhou	2010	Tang N, 2013[45]
	Urumqi	2010-2011	Yi Li Mire A Bu Da Limu, 2013[46]
	Dongying	2011	Zhu Y, 2014[47]
	Guiyang	2012-2013	Yang C, 2014[48]
	Taiyuan	-	Peng L, 2003[49]
	Datong	-	Zhao Q, 2004[50]
	Nanjing	-	Niu H, 2005[51]
	Liuzhou	-	He X, 2005[52]
	Tianjing	-	Wu S, 2005[53]
Soil	Pearl River Delta	2001	Liu G, 2011[54]
	Shunde	2002	Li Y, 2008[55]
	Shantou	2002	Hao R, 2007[56]
	Tianjin	2002	Tao S, 2004[57]
	Pearl River Delta	2002	Cai Q, 2007[58]
	Hangzhou	2002	Chen B, 2004[59]
	Hangzhou	2002	Zhu L, 2004[60]
	Beijing	2004	Wang K, 2009[61]
	Huizhou, Zhanjiang	2004-2005	Ma J, 2011[62]
	Dalian	2005	Wang Z, 2007[63]
	Pearl River Delta	2005	Ma X, 2008[64]
	Qinghai-Tibet plateau	2005-2006	Tao S, 2011[65]
	Qiantang	2005-2006	Zhu L, 2008[66]
	Chengdu	2006	Xing X, 2011[67]
	Shanghai	2006	Jiang Y, 2009[68]
	Shanghai	2007	Liu Y, 2010[69]

	Shenzhen	2007	Cao S, 2010[70]
	Tibetan Plateau	2007	Wang C, 2014[31]
	Guangdong	2007	Wang Y, 2012[71]
	Zhejiang	2007	Li J, 2010[72]
	Karst tiankeng	2007	Wang Y, 2009[73]
	Shanghai	2007	Jiang Y, 2007[74]
	Anhui	2007	Wang R, 2010[75]
	Yunnan	2007	Lv J, 2009[76]
	Huanghuai Plain	2007-2009	Yang B, 2012[77]
	Beijing	2008	Liu S, 2010[78]
	Wenling	2008	Tang X, 2010[79]
	Taizhou	2008	Tang X, 2010[80]
	Beijing	2008	Peng C, 2011[81]
	Benxi	2008	Li F, 2011[82]
	Bohai Sea	2008	Jiao W, 2013[83]
	Datuo karst Tiankeng	2008	Theodore O, 2008[84]
	Karst	2008	Wang Y, 2012[85]
	Liaohe estuarine	2008-2009	Lang Y, 2012[86]
	Hangzhou	2008-2010	Zhong Y, 2013[87]
	Songhua River	2009	Ma W, 2013[88]
	Shenyang	2010	Sun L, 2013[89]
	Jinjiang River	2011	Yang D, 2013[90]
	Shanghai	2011	Wang X, 2013[91]
	Urumqi	2011	Chen M, 2013[92]
	Shanghai	2011	Wang X, 2013[91]
	Hangzhou	-	Yu G, 2014[93]
	Tianjin	-	Li J, 2010[94]
	Jiaxing	-	Zhang Y, 2013[95]
	Yangtze River Delta	-	Ping L, 2007[96]
	Beijing	-	Chen Y, 2004[97]
	Beijing	-	Li X, 2006[98]
	Jiaxing	-	Zhang Y, 2011[99]
	Beijing	-	Peng C, 2012[100]
	Jiaxing	-	Zhang Y, 2011[99]
Freshwater	Jiulong River	1999	Maskaoui K, 2002[101]
	Hangzhou	2002	Zhu L, 2004[60]
	Hangzhou	2002	Chen B, 2004[59]
	Yellow River	2004	Li G, 2006[102]
	Tianjin	2004	Cao Z, 2005[103]
	Jiangsu	2004-2005	He H, 2011[104]
	Yangtze River	2005	Feng C, 2007[105]
	Daliao River watershed	2005	Guo W, 2007[106]
	Xihe River	2005	Guo W, 2011[107]
	Yellow River	2005	Lang Y, 2008[108]

	Yunnan	2007	Lv J, 2009[76]
	Wenzhou	2007	Li J, 2010[72]
	Songhua River	2007	Zhao X, 2014[109]
	Tibet	2008-2009	Chen Y, 2014[110]
	Yangtze River Delta	2009	Shi W, 2013[111]
	Hun River	2009	Zhang H, 2013[112]
	Songhua River	2009	Ma W, 2013[88]
	Yangtze River Delta	2010	Zhang L, 2012[113]
	Jinjiang	2011	Yang D, 2013[90]
	Jiaxing	-	Zhang Y, 2013[95]
Freshwater sediment	Pearl River Delta	1997	Mai B, 2002[114]
	Jiulong River	1999	Maskaoui K, 2002[101]
	Hangzhou	2002	Zhu L, 2004[60]
	Hangzhou	2002	Chen B, 2004[59]
	Shunde, Guangdong	2002	Li Y, 2008[55]
	Yellow River	2004	Li G, 2006[102]
	Haihe River	2004	Bin J, 2007[115]
	Yangtze River	2004	Hui Y, 2009[116]
	Daliao River watershed	2005	Guo W, 2007[106]
	Yellow River Estuary	2005	Lang Y, 2008[108]
	Yellow River	2005	Sun J, 2009[117]
	Yangtze River -Wuhan	2005	Feng C, 2007[105]
	Yellow River - Lanzhou	2005	Yu Y, 2009[118]
	Qiantang	2005-2006	Zhu, L, 2008[66]
	Beijing	2006	Luo J, 2009[119]
	Zha Long wetland	2006	Li J, 2013[120]
	Wenzhou	2007	Li J, 2010[72]
	Huaihe River	2007	Feng J, 2011[121]
	Baiyangdian	2007	Hu G, 2009[122]
	Yellow River Delta	2007	Yang Z, 2009[123]
	Lijiang River	2007	Xue B, 2013[124]
	Songhua River	2007	Zhao X, 2014[109]
	Harbin	2007-2009	Liu Y, 2013[125]
	Huai River	2008	Fu J, 2011[126]
	Taihu	2008-2009	Ji Y,2010[127]
	Tianjin	2009	Lu X, 2012[128]
	Lake Taihu	2009	Zhang R, 2014[129]
	Jialu River	2009	Fu J, 2011[130]
	Songhua River	2009	Ma W, 2013[88]
	Luan River	2009	Cao Z, 2010[131]
	Baohai Sea	2009	Zeng S, 2013[132]
	Haihe River	2010	Liu F, 2013[133]
	Xiangjiang	2010	Zhang L, 2013[134]

	Taihu	2010	Zhang Y, 2012[135]
	Majia-Tuhai	2010	Liu F, 2012[136]
	Dahuofang	2010	Lin T, 2012[137]
	Fenhe	2010	Li W, 2012[138]
	Poyang Lake	2011	Lu M, 2012[139]
Sea water	Western Xiamen Bay	1999	Maskaoui K, 2002[101]
	Pearl River Estuary	2002-2003	Luo X, 2008[140]
	Wenzhou	2007	Li J, 2010[72]
	Dalian Coast	2010	Liu X, 2013[141]
	Jiaxing	-	Zhang Y, 2014[95]
Sea sediment	Pearl River Delta	1997	Mai B, 2002[114]
	Western Xiamen Bay	1999	Maskaoui K, 2002[101]
	Mai Po Inner Deep Bay	2004	Zhao Z, 2012[142]
	Wenzhou	2007	Li J, 2010[72]
	Laizhou Bay	2007	Hu N, 2010[143]
	Liaodong Bay	2007	Hu N, 2011[144]
	Yellow river estuary	2007	Hu N, 2013[145]
	Dalian Coast	2010	Liu X, 2013[141]
	Quanzhou Bay	2011	Yang D, 2013[90]
	Zhanjiang Bay and Leizhou Bay	-	Huang W, 2012[146]
	Liaodong Bay	-	Liu W, 2007[147]
	Qingdao	-	Ma M, 2001[148]
Natural vegetation	Zha Long wetland	2006	Li J, 2013[120]
	Wenzhou	2007	Li J, 2010[72]
Agricultural vegetation	Tianjin	2002	Tao S, 2004[57]

Notes: - means sampling year is not clarified in the paper.

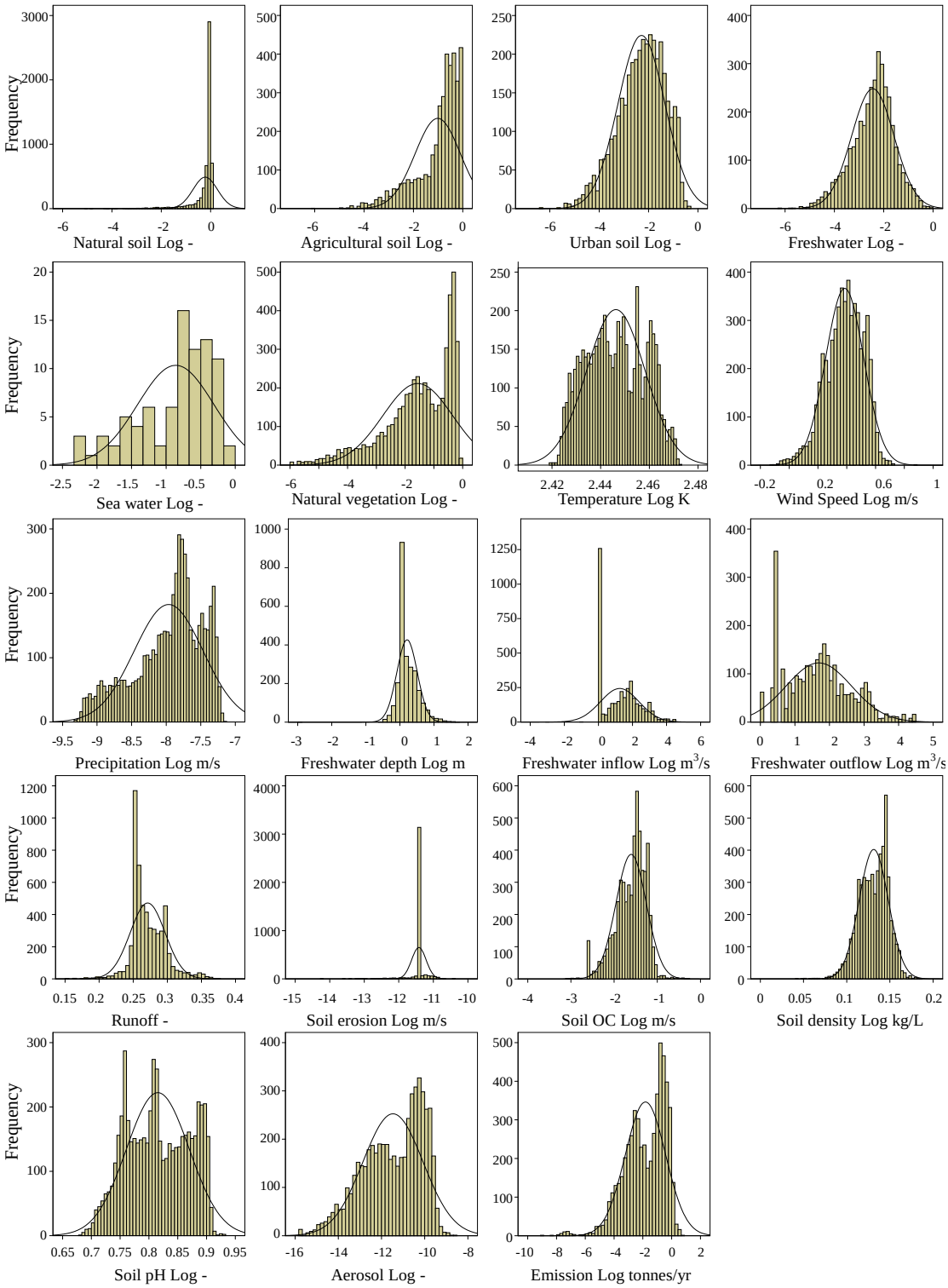

Figure S2. The probability distribution of emission and 18 environmental parameters

Model evaluation results

The probability distribution of the model output by Monte Carlo simulation can be found in Figure S3.

The point-to-point comparison of predicted and observed BaP concentration in agricultural soil, urban soil, sea water and sediment is shown in Figure S4.

Table S5 shows the SCV index output by sensitivity analysis.

By comparing output from SESAMe v3.0 with SESAMe and SESAMe v2.0, it was clear that SESAMe v3.0 provides better match with the measurement data. For SESAMe, the continental scale (the area of the whole territory of mainland China) is too large to affect such relatively small regional cells (200 km squared), as the transport distance of BaP might be only a few hundreds of kilometres; and for SESAMe v2.0, the cell size is less capable to predict extreme values.

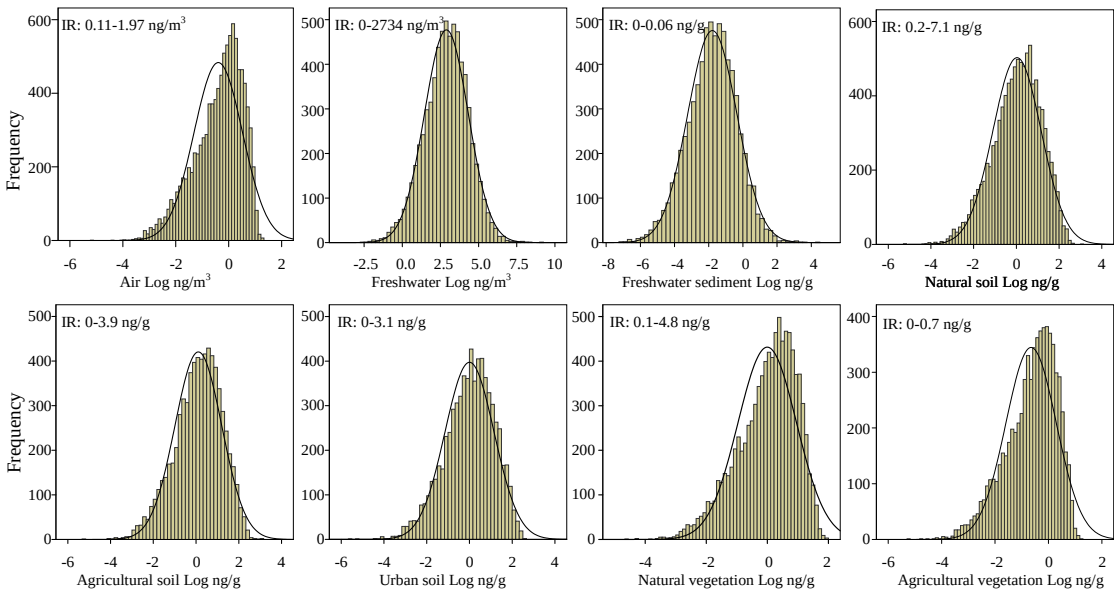

Figure S3. Lognormal distribution and interquartile range (IR) of predicted BaP by Monte Carlo simulation in all media

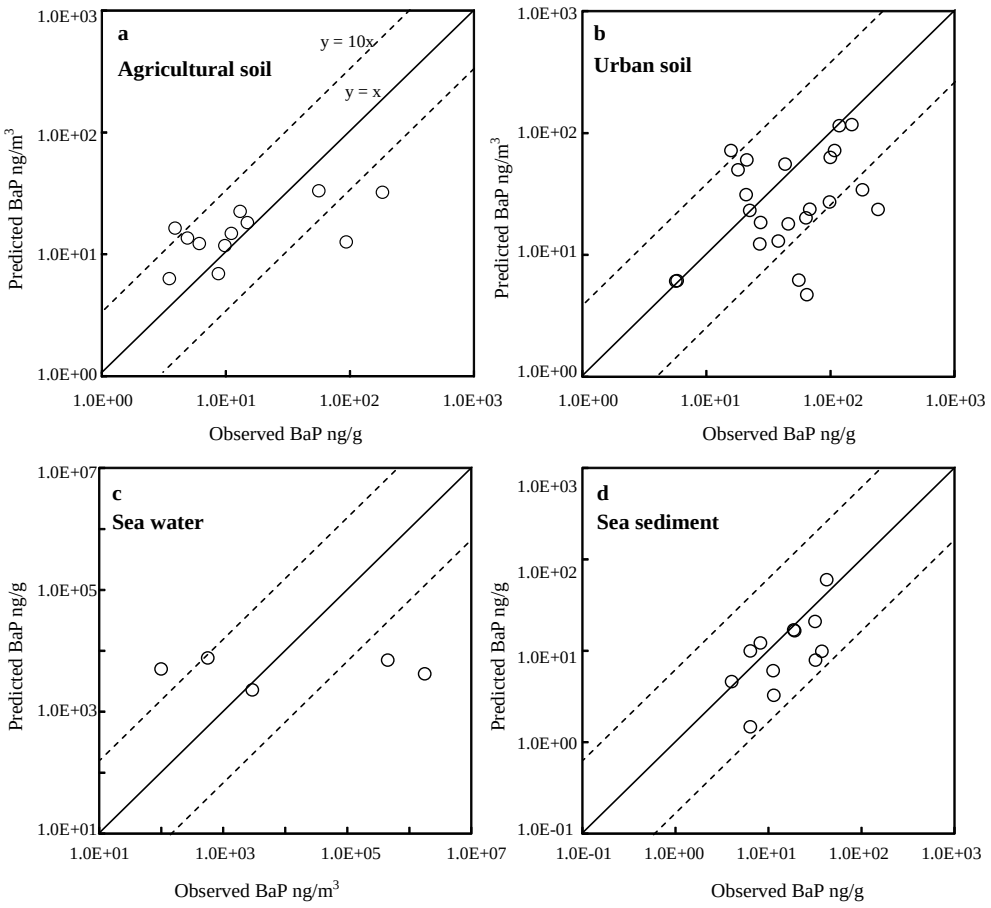

Figure S4. The point-to-point comparison of predicted and observed BaP concentration in agricultural soil, urban soil, sea water and sea sediment (only predicted data with corresponding measured data was used)

Table S5. Index of SCV sensitivity analysis

SCV	Environmental parameters	Regional scale										Continental scale									
		Air	**W1**	**Sed1**	**W2**	**Sed2**	**S1**	**S2**	**S3**	**V1**	**V2**	**Air**	**W1**	**Sed1**	**W2**	**Sed2**	**S1**	**S2**	**S3**	**V1**	**V2**
Regional scale	Area fraction of natural vegetation		0.24	0.25			0.61	0.51	0.50	0.69	0.73		0.13	0.13			0.14	0.16	0.14	0.13	0.11
	Temperature	0.29 (0.16)	1.49 (1.25)	1.86 (1.37)	1.02	1.05	19.33 (3.5)	18.95 (3.45)	19.29 (3.58)	19.35 (4.87)	13.80 (4.87)	0.25 (0.14)	0.76 (0.36)	0.70 (0.4)	3.82 (0.88)	3.72 (0.9)	0.23 (0.22)	(0.21)	0.23 (0.21)	0.18 (0.20)	0.12
	Wind speed	0.13	0.73	0.82	0.18	0.17	0.74	0.72	0.74	0.50	0.39						0.10		0.10		
	Precipitation	0.13	9.31	9.74	0.46	0.43	7.45	7.44	7.36	5.45	5.99		1.21	1.25	4.11	0.84	0.35	0.18	0.35	0.18	
	Surface water depth		3.64	3.98									0.68	0.68	0.31	0.33		0.19			
	Water inflow		0.29	0.22									0.16	0.16							
	Water outflow		1.86	1.91	0.15	0.15															
	Runoff		0.50	0.41	0.19	0.18							2.55	2.53	1.15	1.19		0.89			
	Soil water erosion rate							0.23							0.11						
	Soil OC		1.95	1.40	5.89	5.76	0.28	0.18	0.21				0.25	0.14	3.98	3.89					
	Soil Density		1.57	1.22											0.27	0.41					
	Sediment OC			0.48																	
	Soil pH																				
	Volume fraction of aerosol	0.50	0.19	0.15	0.39	0.39	1.44	1.47	1.42	1.61	2.53	0.45	0.14	0.14	0.13	0.14					
	Emission	0.10			1.96	1.96		0.10	0.10				0.12	0.12							
Continental scale	Area fraction of natural vegetation														0.45	0.47				0.12	0.24
	Temperature	0.53 (0.43)	(3.22)	1.29 (3.43)			(1.21)	(1.2)	(1.2)	0.28 (1.2)	0.39 (1.2)	0.51 (0.44)	29.72 (3.7)	29.20 (3.4)	62.45 (3.0)	60.79 (3.25)	17.56 (3.55)	24.43 (3.52)	17.63 (3.47)	13.33 (2.79)	7.65 (2.79)
	Wind speed																				
	Precipitation		0.60	0.53			0.16	0.16	0.15	0.28	0.32		6.19	6.24			0.24	1.61	0.17	0.85	0.66
	Surface water depth		0.25	0.22									0.50	0.50				0.15			
	Runoff		0.20	0.19									0.17	0.18							
	Soil water erosion rate		0.11										0.78	0.79	1.88	1.96		0.65			
	Soil OC		31.14	28.70	0.12	0.11							35.99	36.19	0.71	0.94	1.25	13.27	1.02		
	Soil Density		1.54	1.42									3.11	1.00	0.54	1.16		0.87			
	Sediment OC		0.28	0.24									0.84	1.04				0.27			
	Soil pH																				
	Volume fraction of aerosol	0.20	0.11									0.19	0.69	0.69	0.37	0.43	0.32	0.46	0.32	0.13	0.18
	Emission	0.41	1.25	1.17	0.51	0.55	4.79	4.92	4.73	2.51	1.93	0.50	2.64	2.60	1.21	1.31	2.63	3.05	2.64	2.01	1.42

Notes: the SCV index in brackets for temperature is the SCV of temperature without considering the temperature-dependent degradation rates.

BaP transport and partitioning between media

The net flux of BaP between media and the runoff flux from soils to freshwater are shown in Figure S5. A diagram of the log-transformed BaP flow rate between media is indicated in Figure S6.

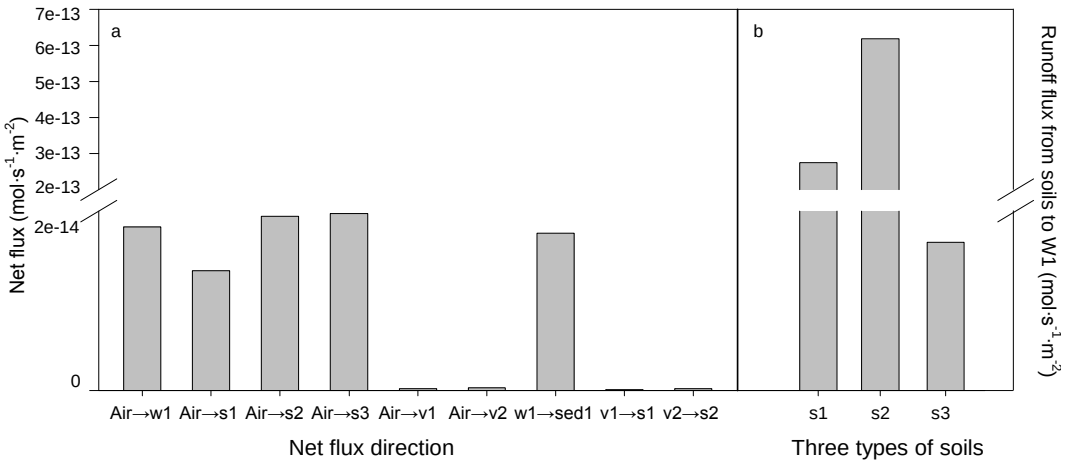

Figure S5. Net flux at the interface of environmental compartments (a) and runoff and erosion flux from three types of soils to surface freshwater (b); w1, surface freshwater; sed1, freshwater sediment; s1, natural soil; s2, agricultural soil; s3, urban soil; v1, natural vegetation; v2, agricultural vegetation; '→' indicates the direction of the net flux between two media.

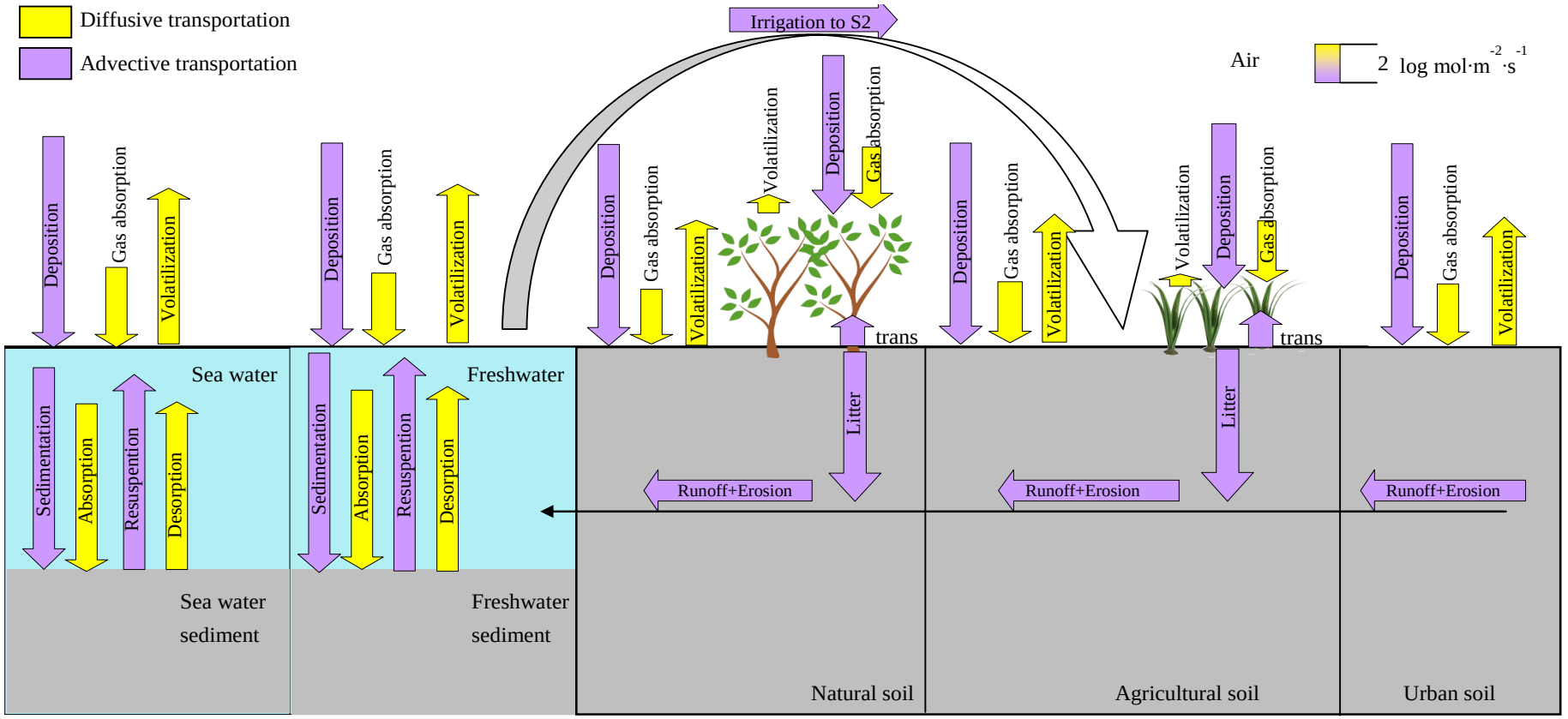

Figure S6. The diagram of the log-transformed BaP flow rate between media at the interface; S2, agricultural soil; trans, transpiration; erosion is water erosion

The spatial distribution of BaP

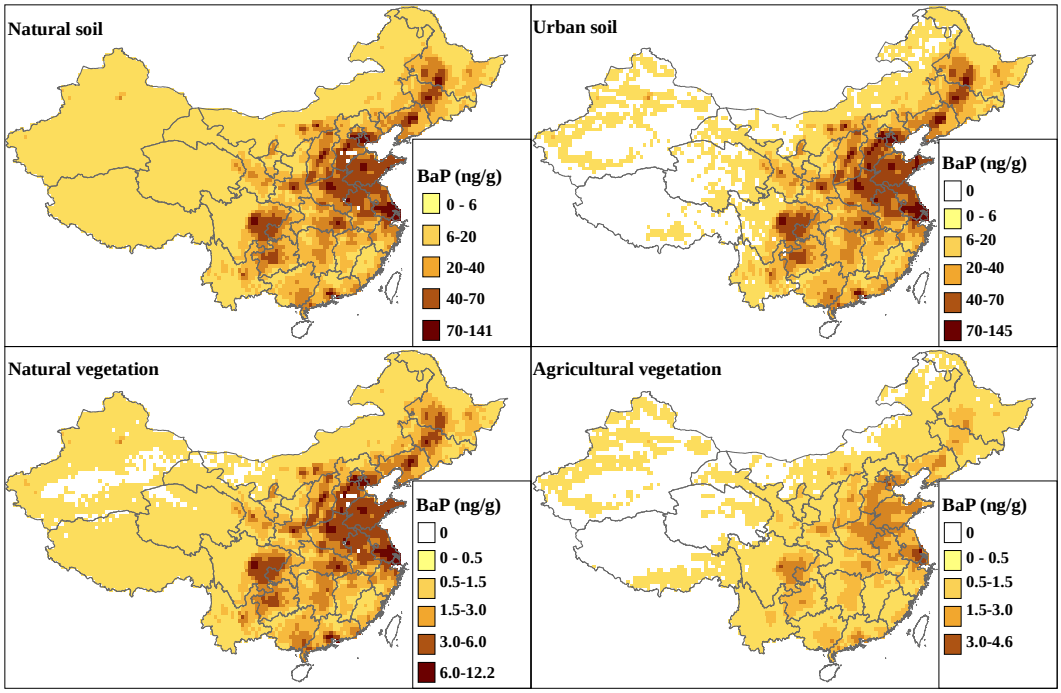

Figure S7. Predicted BaP distribution in natural and urban soil, natural and agricultural vegetation

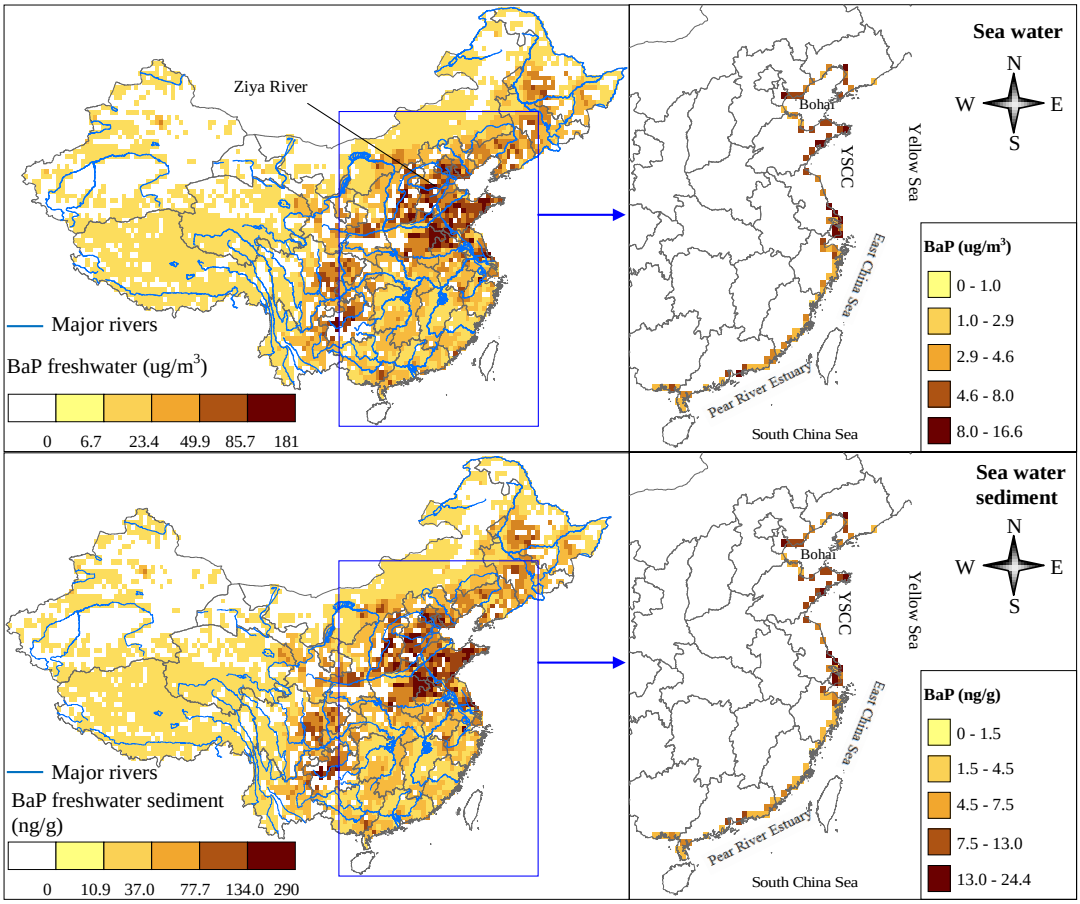

Figure S8. Predicted BaP distribution in freshwater and sediment, sea water and sediment

Future scenarios

In the future emission scenarios, a method by Bond et al[149] was adopted, which describes the fraction of the technology used in the activities of individual emission category over time with technology transition. The method is defined in equation (8) below.

$$X(t) = (X_0 - X_f)e^{(-(t-t_0)^2/2S^2)} + X_f \quad (8)$$

where X_0 and X_f are the initial and the final fraction of a technology, which are usually one and zero respectively for polluting technologies being phased out; $X(t)$ is the fraction at time t; t_0 is when the technology transition starts; and S is a rate.[149] Table S6 provides the categories of emission sources and activities considered in the two future emission scenarios (Sc1 and Sc2), and the corresponding t_0 and S.[16] The fractions of different technology for the year 2007 and 2030 have been calculated in this way to estimate the future reduction of BaP emission from these sources in Table S6.

Table S6. Emission sources considered in Sc1 and Sc2 with the corresponding technologies[16]

Scenarios	Sources	Technologies	X(t)	t_0	S
Sc1	Coal consumed in energy production	a. unconrolled stack b. controlled stack	a/(a+b)	1979	18
	Coal consumed in industry	a. unconrolled stack b. controlled stack	a/(a+b)	1979	25
Sc2	Indoor firewood burning	c. traditional stove d. improved stove	c/(c+d)	1985	23
	Indoor crop residue burning	c. traditional stove d. improved stove	c/(c+d)	1988	21

EFs have been assumed to be stable over time for each technology in Table S6. So the reduced emission can be calculated. Figure S9 shows the predicted BaP background concentration in freshwater in 2007 as the base year and in 2030 under different scenarios.

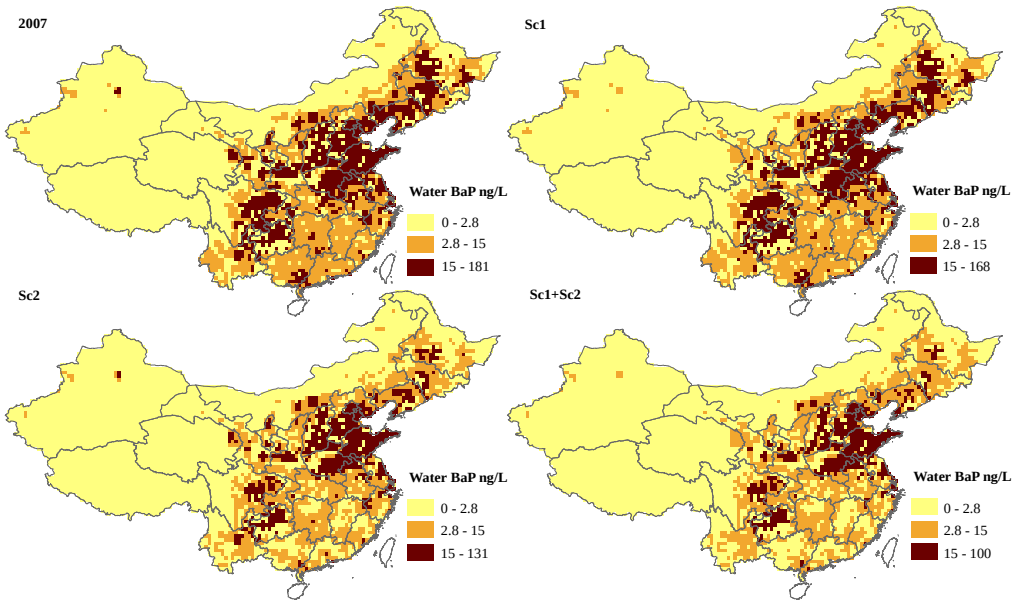

Figure S9. BaP freshwater concentration in 2007, Sc1, Sc2 and Sc1+Sc2

Figure S10 reflects the importance of the emission controls for both the central grid cell and the surrounding area. Sc2 is the scenario 2 discussed in the main paper, in which the emission to continental scale is reduced correspondingly as the emission to the grid cells that it covers is reduced. "Sc2-unchanged continental emission" assumes that when the emission to an individual grid cell is reduced its continental emission remains the same level as that in 2007. This scenario can be used to investigate the efficiency of pollution control measures if only the regional emission is controlled/reduced but without any corresponding reduction in surrounding regions. This could possibly happen when pollution management is only implemented in one city or province.

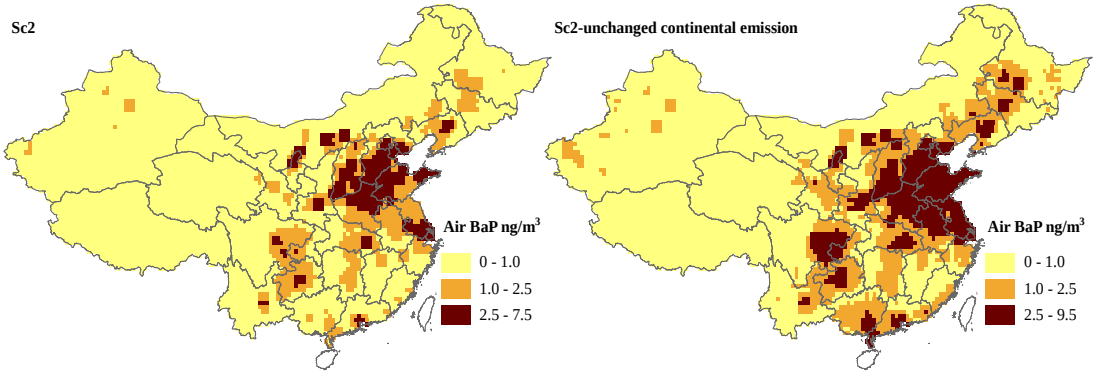

Figure S10. Comparison of different emissions scenarios for the continental scale; In Sc2, emission to the continental scale is correspondingly reduced; Sc2-unchanged continental emission, emission to the continental scale remains the same as that in 2007 and only emission to regional scale is reduced.

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III

A multimedia fate model to support chemical management in China: a case study for selected trace organics

Ying Zhu[1], Oliver R. Price[2]*, John Kilgallon[2], Cecilie Rendal[2], Shu Tao[3], Kevin C. Jones[1], and Andrew J. Sweetman[1]*

[1]Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, United Kingdom

[2]Safety and Environmental Assurance Centre, Unilever, Sharnbrook MK44 1LQ, United Kingdom

[3]Laboratory for Earth Surface Processes, College of Urban and Environmental Sciences, Peking University, Beijing 100871, China

*Corresponding author email:

Andrew J. Sweetman, a.sweetman@lancaster.ac.uk

Oliver R. Price, Oliver.Price@unilever.com

Abstract

SESAMe v3.3, a spatially explicit multimedia fate model for China, is a tool suggested to support quantitative risk assessment for national scale chemical management. The key advantage over the previous version SESAMe v3.0 is consideration of spatially varied environmental pH. We evaluate the model performance using estimates of emission from total industry usage of three UV filters (benzophenone-3, octocrylene and octyl methoxycinnamate) and three antimicrobials (triclosan, triclocarban and climbazole). The model generally performs well for the six case study chemicals as shown by the comparison between predictions and measurements. The importance of accounting for chemical ionisation is demonstrated with the fate and partitioning of both triclosan and climbazole sensitivity to environmental pH. The model predicts ionisable chemicals (triclosan, climbazole, benzophenone-3) to primarily partition into soils at steady state, despite hypothetically only being released to freshwaters, as a result of agricultural irrigation by freshwater. However, further model calibration is needed when more field data becomes available for soils and sediments and for larger areas of water. As an example, accounting for the effect of pH in the environmental risk assessment of triclosan, limited freshwater areas (0.03% or ca. 55 km^2) in mainland China are modelled to exceed its conservative environmental no-effect threshold. SESAMe v3.3 can be used to support the development of chemical risk assessment

methodologies with the spatial aspects of the model providing a guide to the identification regions of interest in which to focus monitoring campaigns or develop a refined risk assessment.

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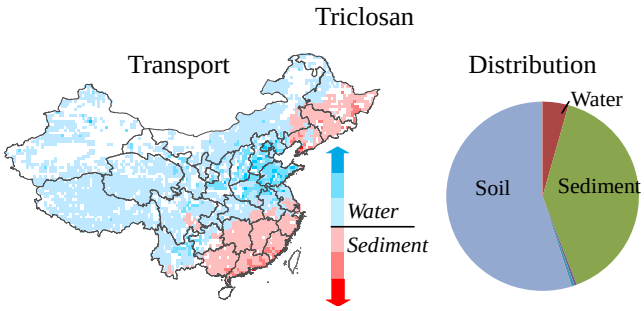

Introduction

Assessment of exposure pathways, relative risk, prioritization and risk management are key for better characterising chemicals and managing potential risks to humans and the environment.[1, 2] For chemical management in China, attention is often currently focused on new chemicals (i.e. newly manufactured or imported) and trace organics that are used or can enter the environment as a common part of our daily life. Examples include active pharmaceutical ingredients, personal care product ingredients (PCPs), endocrine-disrupting chemicals, disinfection by-products and some industrial chemicals etc.[3] Several categories of trace organics can be released directly to the environment after use, or via wastewater treatment plants (WWTPs) to aquatic environments with sewage effluent as well as to soil via the application of irrigation water or sludge. Some may be ionisable, and so have different partitioning behaviour from neutral chemicals after being released.

For better chemical regulation and environmental and health protection, the European Union (EU) and the US have both introduced legal frameworks, EU REACH (2007, Registration, Evaluation, Authorisation and Restriction of Chemicals)[1] and US TSCA (1976, Toxic Substances Control Act).[4] Multimedia environmental fate models have been widely adopted by developed countries in frameworks for chemical management (e.g. EUSES, US PBT Profiler and OECD chemical screening tool etc.),[5-7] and have been demonstrated to be useful decision-support tools.[7, 8] China has so far lagged behind on many aspects of chemical management. However, as a rapidly industrialising country with a large population, the increasing use and release of trace organics has raised questions as to their potential impacts or otherwise on the environment and human health. The Ministry of Environmental Protection (MEP) of China has published the Provisions on the Environmental Administration of New

Chemical Substances in China (edition 2010)[9] to require the registration of new chemicals with relevant risk assessment information. There is therefore a research need to develop a multimedia fate model specifically for China to support the regulation[2] and there is the opportunity for China to exert leadership in the use and adoption of state-of-the-art modelling approaches.

A further development of the SESAMe model,[10, 11] SESAMe v3.3, is presented in this study to account for spatially variable surface water and soil pH values and chemical ionisation, so that ionisable chemicals can be included in model predictions for aiding chemical management for China. Three antimicrobials agents and three UV filters (i.e. triclosan (TCS), triclocarban (TCC), climbazole, benzophenone-3 (BP-3), octocrylene (OC) and octyl methoxycinnamate (OMC)), covering a range of physico-chemical properties were selected for a case study in China to: (1) predict spatially varied environmental concentrations and partitioning in environmental media, (2) demonstrate the importance of accounting for ionisation and environmental pH in chemical risk assessments and (3) illustrate the application of SESAMe v3.3 for chemical management in China. These substances represent chemicals where there are common challenges for modellers and risk assessors, to estimate use and release to the environment from diffusive everyday activities.

Methods and materials

Chemicals selection and properties

Chemical and environmental properties have been demonstrated to determine the chemical fate.[11] Figure 1 shows a chemical space plot indicating the equilibrium partitioning of chemicals in air, water and sediment dictated by logD/Kow (octanol-water partition coefficient for respectively ionisable chemicals and neutral molecules) and logKaw (Henry's Law constant for neutral molecules). Error bars show the extent of the effect of water pH on chemical partitioning between water and sediment (logD calculation see Supporting Information) on example chemicals (142 antimicrobial agents and 19 UV filters) used in commerce (chemical properties predicted mostly by Pipeline Pilot[12]). Water pH also affects the ionisable chemical partitioning between air and water, which is not discussed in this study (Supporting Information). Extreme chemicals with logD/Kow around -12 and logKaw < -20 $Pa \cdot m^3/mol$ almost entirely distribute into a single compartment; while moderate chemicals with logD/Kow between 0 and 10 or logKaw between -10 and 5 $Pa \cdot m^3/mol$ tend to distribute in multiple compartments. .Other environmental parameters may also impact on this distribution (e.g. soil pH) but are not shown in Figure 1.

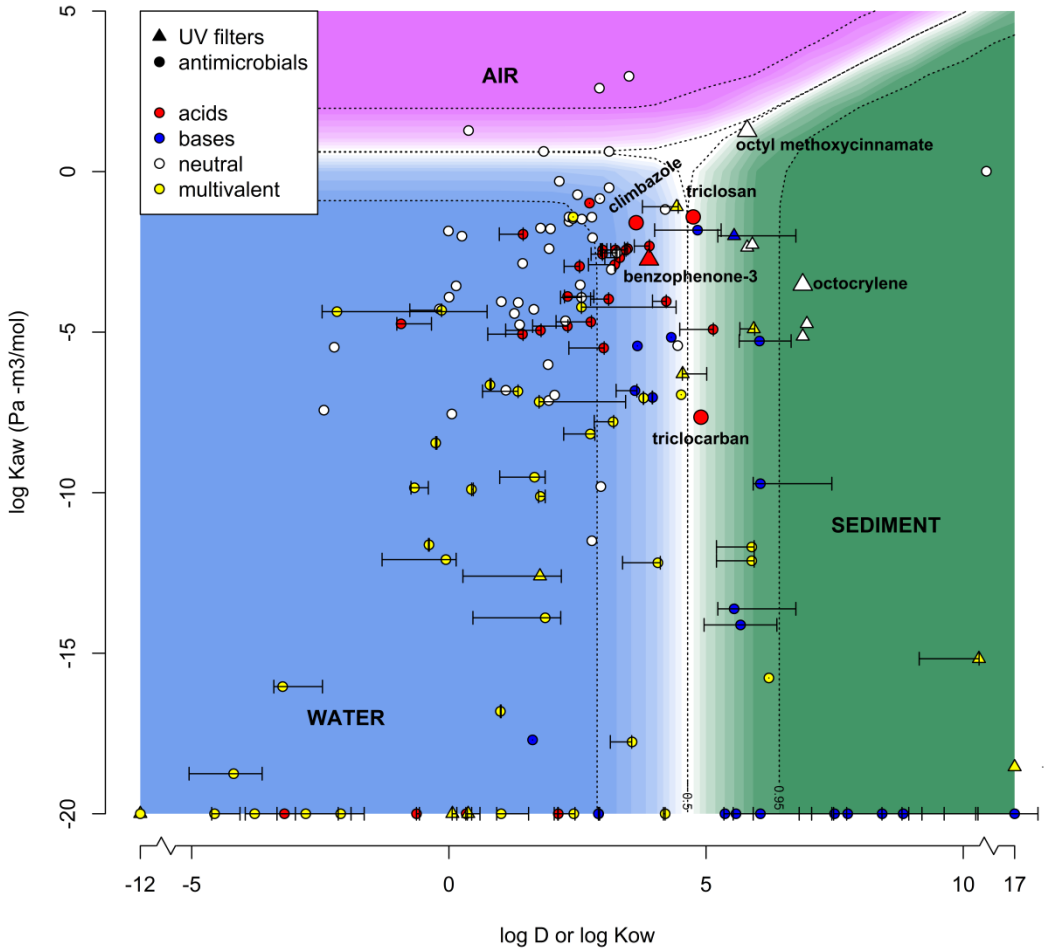

Figure 1 Chemical space plot indicating equilibrium partitioning characteristics of chemicals in air, water and sediment as dictated by logKaw (Henry's Law Constant for neutral molecules at pH = 7) and logD/Kow (octanol-water partition coefficient), which is not generated by SESAMe v3.3; the dotted lines indicate 50% and 95% partitioning into the respective compartments; circles represent antimicrobial agents and triangles are UV filters; Error bars show the range of logD for ionisable chemicals for extremes of measured environmental pH (5.7 – 10.5).

The six case study chemicals (highlighted in Figure 1) were selected from a portfolio used by the PCPs industry covering neutral and ionisable chemicals.[13, 14] Antimicrobial agents and UV filters are two commonly used groups of PCPs. They have been detected in multiple media in different regions across China.[15] UV filters are ingredients used in sunscreen products or cosmetics for protection against the adverse effect of ultraviolet radiation;[16] antimicrobial agents can be used in consumer products to protect against certain types of bacterial or fungi. The lifetime exposure of aquatic organisms to these substances can be sustained regardless of their persistence, when they are continuously discharged into the aquatic environment. Although the ecotoxicity of these chemicals has been studied and observed in acute or chronic exposure tests under high testing concentrations,[16, 17] the environmental measurements or

modelling results generally indicates concentrations below the level of concern.[18] However, these chemicals have 'intermediate' physicochemical properties (Table S1) and can partition into multiple environmental compartments, which makes them ideal case study chemicals. TCS and climbazole are acids with pKa values of 7.9 and 7.5, which are in the range of pH for freshwaters and soils in China (stated below); and BP-3 and TCC are acids with high pKa of 9.54 and 12.7. BP-3 has a lower logKow than TCC; and OC and OMC are hydrophobic neutral chemicals with relatively high logKow values (6.9 and 5.8), which are more likely to be adsorbed to sediment.

Model configuration and evaluation

So far, multimedia chemical fate models used to simulate real environments have typically focussed on neutral organic chemicals. To account for the different partitioning behaviour of ions, it requires chemical ionisation to be considered in the model and the range and variability of pH in the Chinese environment. SESAMe v3.3 (a level III spatially explicit model with a 50×50 km^2 grid) was therefore developed and updated from SESAMe 3.0[10] to incorporate spatial pH data for freshwater and sediment across China (model feature see Supporting Information). The spatial freshwater pH dataset was generated using weekly pH data from 99 gauging stations in China in 2012 (details see Supporting Information).[19] It ranged from 6.8 to 8.6 across China with a median of 7.8 (Figure S1). The pH of solid phases in sediments was assumed to be 0.6 lower than that in freshwater within the same grid cell.[20] Agricultural soil pH values ranged from 4.8 to 8.5 with a median of 6.5 (Figure S2). As with SESAMe v3.0, agricultural soil irrigation by freshwater in the same grid cell was an important process for the transport of compounds from water to soil, during which ca. 370 billion m^3 water was assumed to be uniformly distributed to agricultural soil across mainland China, as described previously by Zhu et al.[10] Other environmental parameters have been introduced previously.[10]

Emissions were assumed to be all released to freshwater. The model was used to predict the spatial concentration of chemicals in environmental media, especially aquatic systems, total mass of chemicals in each environmental compartment and net fluxes between freshwater and sediment at steady state, to show the spatial variation in transport behaviour and distribution. The neutral TCS concentration was predicted to provide a pH adjusted environmental risk assessment for China. Measured data for freshwater and sediment in China were collated from peer-reviewed literature for the six chemicals to evaluate the model (Figure S5 and Table S5). No measured data for UV filters in freshwater sediment was found, however these chemicals are highly insoluble and sorb strongly to organic material on sediment solids which will likely result in low bioavailability and toxicity in the environment.[18] Statistical

distributions of predicted and measured concentrations in freshwater and sediment for China were compared. For individual catchments, as literature on monitoring data was limited and measurements for individual sampling sites was not normally provided, average measurement were compared with average predicted concentration for grid cells covering the catchment. Model uncertainty for each chemical was explored by Monte Carlo simulation by running the model 10,000 times with parameters randomly taken from the environmental parameter and the emission databases. Sensitivity analysis was implemented by adopting a variability-based sensitivity coefficient (SCV, see Supporting Information).

Emission inventory

Emissions are principle model inputs for predicting chemical concentrations. The six chemicals are frequently used formulation ingredients, but their emissions/discharges cannot be readily acquired directly. Therefore a spatially resolved emission inventory was developed, for which chemical specific inclusion levels in products and removal ratios in WWTPs were collected or estimated.

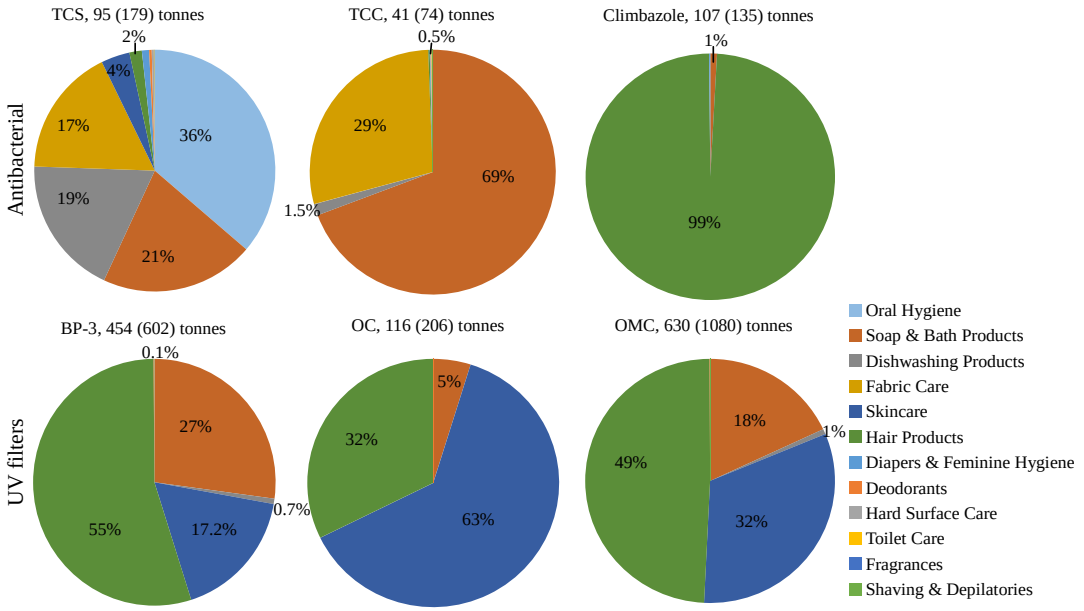

Figure 2 Estimated source composition and total emission and usage (in the brackets) of three antimicrobial agents (TCS, TCC and climbazole) and three UV filters (BP-3, OC and OMC) in China in 2012 as shown after acronym of each chemical above the pie chart

Usage. The Mintel Global New Products database[21] provided i. the (sub-)categories of personal and home care products in the Chinese market; ii. the total number of variants (products by different manufacturer with same function) released on to market under each sub-category; iii. the number of variants with each of the six chemicals under each sub-category. This provided the fraction of products containing specific chemicals. The tonnage

of products sold in the Chinese market was exported from the Euromonitor database.[22] Figure 2 shows the categories of products which contain some or all the six chemicals, which will ultimately be released to the wastewater system. Inclusion levels of chemicals for each sub-category were collected from the literature (Table S2). Combining the above information, the usage of individual chemicals in the Chinese market for 2012 was estimated. Subsequently, it was allocated to counties across China, by linking estimates of product usage at the population level (based on a population's ability to purchase individual products) with spatial distributions of GDP across China.[23]

Emissions. All products sold in the Chinese market in 2012 were assumed to be consumed and released with the domestic wastewater within the same year. Due to uneven socioeconomic development, the proportion of population connected to WWTPs for wastewater treatment varied between urban and rural areas and also between different counties. The proportion of population connections to WWTPs for urban and rural areas were estimated based on the per capita daily domestic water use, the domestic wastewater discharge and the rural and urban population data at the province level (details see Table S3 and Supporting Information). Owing to a lack of data, urban and rural per capita water use was assumed to be equal and the estimated proportion of population connection to WWTPs was assumed to be the percentage of wastewater processed by WWTPs and assigned to each county.

The measured removal ratios of the six chemicals in WWTPs taken from the peer reviewed literature ranged from 55->97% for TCS,[24, 25] 96-98% for TCC,[26] 18-67% for climbazole,[27, 28] 10-99% for BP-3,[29-31] 40-99% for OMC [30-32] and 36-99% for OC.[31-33] The variation of values for each chemical is due to different sampling seasons and methods or WWTP technologies in different studies. To aid the selection of a representative value for a secondary activated sludge plant (which is the typical wastewater technology in China), the SimpleTreat 3.2 model,[34] which can model ionisable chemicals, was used. The predicted values were typically within the removal ratio ranges from the literature and were considered reasonable and thus used in the SESAMe model. The predicted removal ratios were 95% for TCS, 96% for TCC, 89% for OMC, 91% for OC and 49% for BP-3. For climbazole, the predicted value was 12% and beyond the measured range (reasons see Supporting Information), so a measured value of 40% from a study in Beijing[27] was assumed.

The emissions of the six chemicals by county were calculated combining the usage, chemical removal ratio in WWTPs and the fraction of domestic wastewater treated by WWTPs. This estimation method is not limited to the six chemicals but can be used for most PCP chemicals.

The emissions by county were allocated by population to the 50×50 km^2 grid using ArcGIS 10.2.2.

Correcting for pH dependent toxicity

For ionisable chemicals, toxicity has been demonstrated to be pH dependent.[35, 36] However, current toxicity data or standard guidelines on such chemicals are suggested without pH correction or pH conditions, which may cause high uncertainty for environmental risk assessments. For example, 100 ng/L of total TCS was the recommended standard by the UK Technical Advisory Group on the Water Framework Directive for long-term exposure in freshwater but without suggesting the applicable environmental pH;[37] the PNEC (predicted no effect concentration) of TCS was reported to range from 26.2 to 1550 ng/L as total TCS concentration,[35, 38-40] probably due to uncertainties and variability in pH during toxicity studies, which typically increased (7.5/7.7 to 8.65/10.2) in the growth media during the algal test due to photosynthesis.[35, 41] This range of values may also have resulted from other factors such as the measurement system used or analytical measurement errors, etc. It was demonstrated that where strictly controlled pH conditions were used, the effective component for toxicity (i.e. neutral TCS) should have relatively constant concentration in toxicity test with daphnia[35] and algae[42] (Table S4).

Therefore, a pH-corrected indicator of $PEC_n/PNEC_n$ (PEC, predicted environmental concentration; the subscript 'n' indicates the neutral concentration) was developed for ionisable chemicals to better account for toxicity in the environment and ultimately a more realistic environmental risk assessment. TCS was selected as an example, as it is well studied with a large toxicity dataset.[41] $PNEC_n$ in freshwater can be derived by the same method for PNEC - $NOEC_n/EC_{n,X}$ (x, 5-20%) of a most sensitive aquatic species to TCS (i.e. certain algae)[16, 17] divided by the assessment factor (AF).[43] $NOEC_n$ was calculated using NOEC at different pH levels reported by Roberts et al.,[42] as the pH in exposure growth media was well controlled in this study (Table S4). The lowest $NOEC_n$ (1.5 μg/L) was used to calculate the $PNEC_n$ for freshwater as a conservative estimation for environmental quality, by which a $PNEC_n$ of 150 ng/L was estimated with an AF of 10. PEC_n across mainland China was predicted using SESAMe v3.3. It should be noted that such an indicator is only suggested for weak monovalent acids and bases that are mostly present in neutral forms; and the toxicity of multivalent acids or bases in water are more complex which are not considered here.

Results and discussion

Emission inventory

Figure 2 shows the total emissions and usage (in brackets) (the units are tonnes) estimated to be 95 (179) for TCS, 41 (74) for TCS, 107 (135) for climbazole, 454 (602) for BP-3, 116 (206) for OC and 630 (1080) for OMC in mainland China for 2012. Oral hygiene (36%), soap & bath products (21%), dishwashing (19%) and fabric care products (17%) comprise the main sources of TCS; soap & bath products (69%) are the main sources of TCC; climbazole is mainly used in hair products (99%) as an anti-dandruff agent. OC is mostly used in skincare products (63%) including daily face care (usage 47 tonnes) and sun care products (usage 80 tonnes), as it is more photo-stable than the other UV filters and can stabilize the other UV filters in the formula;[44] in contrast, hair products are the dominant category for BP-3 (55%) and OMC (49%); soap & bath products are an important source for BP-3 (27%) and fragrances are an important source for OMC (32%).

The emission and usage in this study for 2012 are respectively ca. 1.5 and 1.8 times higher for TCS[45] but less than half for climbazole[46] of those estimated for 2011 by Zhang et al. Although product consumption will probably increase every year in China along with the economic growth, it is still unlikely that the usage/emission of TCS could increase significantly over a year. As an important category of products consumed in the Chinese market, the consumption of fabric care products (power/liquid detergents) is probably greatly underestimated (431 t/year)[45] by Zhang et al. For climbazole, the fraction of variants for shampoo that contain this chemical in our study (1.15%) is estimated to be lower than that by Zhang et al. Uncertainty may exist in usage and emission estimation for these chemicals, because (1) it remains challenging to obtain total industry usage and estimate a more accurate wastewater connectivity to WWTPs in China; (2) the lack of information, the inclusion level is assumed to be constant for all variants under the same category and the removal ratio is assumed to be identical in all WWTPs across the country for individual chemical, which are probably not a reflection of reality.

Figure S3 shows total emissions by county across China (exclusive of Taiwan) in 2012 for the six selected chemicals. The ranges (5^{th}-95^{th} percentiles) plus median are 0.001-0.11 (median, 0.02) tonnes TCS, 0.0004-0.05 (0.01) TCC, 0.002-0.12 (0.03) climbazole, 0.007-0.5 (0.1) BP-3, 0.001-0.14 (0.02) OC and 0.01-0.75 (0.14) OMC. Generally, emissions of all six chemicals are relatively high in highly populated regions in Liao River basin in Liaoning, North China Plain (NCP), Jiangsu, Shanghai, north Zhejiang, eastern Sichuan, coastal regions in Fujian and Guangdong. Several regions in Guangdong province (e.g. Dongguan, Guangzhou, Shenzhen and Foshan etc.) and Shanghai have the highest emission of all six chemicals, followed by Beijing. The lowest usage and emission for six chemicals is in Cuoqin in Tibet. Figure S4 shows the emissions allocated to 50×50 km^2 grid.

Model evaluation and spatial distribution of the six chemicals

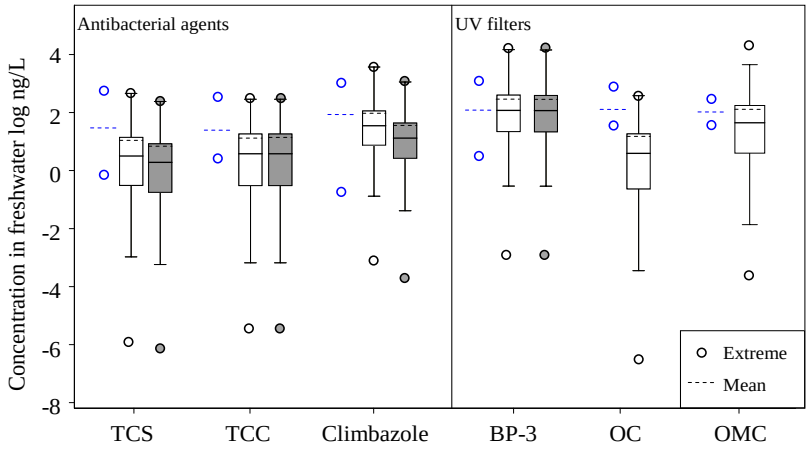

Figure 3 Boxplot (SPSS 18) of predicted total and neutral chemical concentrations (predictions for all grid cells), and measurements in freshwater (blue). White-box group indicates predicted total chemical concentrations (neutral plus ionic molecules); grey-box group indicates predicted neutral concentrations; the horizontal solid line in the box is the median; top and bottom of the box are respectively the 75th and 25th percentiles; the top and bottom of the whisker are respectively the highest and lowest case within 1.5 times the interquartile range. Extreme circles are max/min values.

The model generally performs well for the six chemicals as shown by the comparison between predictions and measurements (Figure 3, S6-S7). Predictions cover a broader range of concentrations than measurements, especially for lower concentrations, as measured data are only available for several major catchments with higher emissions in more densely populated regions (Figure S5). In addition, in the Chinese aquatic environment, the four ionisable chemicals mostly exist in neutral form, although concentrations of neutral molecules are significantly less than total concentrations for TCS and climbazole with lower pKa values. Figure S7 shows the comparison between measurements and predictions for each catchment, with differences within 2 orders of magnitude, which is a reasonable agreement for these types of model predictions.[47] The differences are probably a reflection of the model calculating the average concentration of the individual 50×50 km^2 grid cell in contrast to measurements representing an instant on-site level. Therefore, larger sample sizes relative to the catchment area which cover both mainstream and tributaries would probably ensure a better match with model predictions, e.g. TCS and TCC (Table S5). For climbazole in the Yangtze River, as the sample size (n=27) was relatively low compared to the large area of the river basin, a greater difference is shown between measurements and predictions. Results of the sensitivity analysis are shown in Table S6. The distribution of chemical concentrations in freshwater and sediment using Monte Carlo simulation is lognormal and is shown in Figure

S8, along with the interquartile range. Further model calibration is needed when more field data becomes available for soils, sediments or for larger areas of water.

A range of concentrations (5^{th} - 95^{th}, plus median in brackets) are predicted in freshwater and sediment as follows (Figure S9-S10): freshwater, 2.3×10^{-4} - 71 (3) ng/L for TCS, 4.0×10^{-4} - 57 (4) ng/L for TCC, 0.03 - 334 (35) ng/L for climbazole, 0.05 - 1209 (118) ng/L for BP-3, 7×10^{-5}-74 (4) ng/L for OC and 0.004 - 634 (44) ng/L for OMC; freshwater sediment, 8×10^{-5} - 25 (1.2) ng/g for TCS, 1.5×10^{-3} – 183 (13) ng/g for TCC, 6×10^{-4} - 13 (1.3) ng/g for climbazole, 2×10^{-3} - 56 (6) ng/g for BP-3, 4×10^{-4} - 250 (14) ng/g for OC and 4×10^{-3} - 386 (29) ng/g for OMC. The chemicals present in sediment are mostly predicted to be adsorbed on solids rather than in pore water especially for high logKow chemicals. As a result of the freshwater irrigation in agricultural production, predictions show the range of concentrations (5^{th} - 95^{th}, plus median in brackets) in agricultural soil across mainland China as 3×10^{-9} – 0.2 (0.008) ng/g for TCS, 3×10^{-11} – 0.1 (0.01) ng/g for TCC, 5×10^{-10} – 0.7 (0.1) ng/g for climbazole, 2×10^{-10} – 1.7 (0.2) ng/g for BP-3, 3×10^{-8} – 0.04 (0.003) ng/g for OC and 1.5×10^{-8} – 0.4 (0.03) ng/g for OMC. The difference with estimated emissions for TCS and climbazole between this study and those by Zhang et al.[45, 46] is in the same order of magnitude. However, this study predicts much broader concentration ranges for the two chemicals in both freshwater and sediment than those by Zhang et al. (Table S7), probably as the finer resolution of SESAMe v3.3 can identify extreme values better. Model predictions also indicate a chemical input to coastal seawater system (predicted concentrations see Supplement Information).

Generally, the spatial distribution patterns of concentrations for the six chemicals are similar and also match those of estimated emissions at the national scale. For all chemicals, regions in the NCP, Liao River basin in Liaoning, Jiangsu and coastal area in Zhejiang, Fujian and Guangdong have higher concentrations than other regions, which also have higher emissions due to high population density. Also the high concentration in NCP is probably related to the low river discharge there. Regional contrasts exist between emissions and concentrations mainly due to the discharge flow, e.g. regions that have the highest emissions in Guangdong and Shanghai do not have the highest concentrations in freshwater and sediment as a result of the dilution by large discharge flows; whilst western and northern Guizhou do not have very high emissions but have relatively high concentrations due to low discharge flow.

Chemical fate and partitioning among environmental media

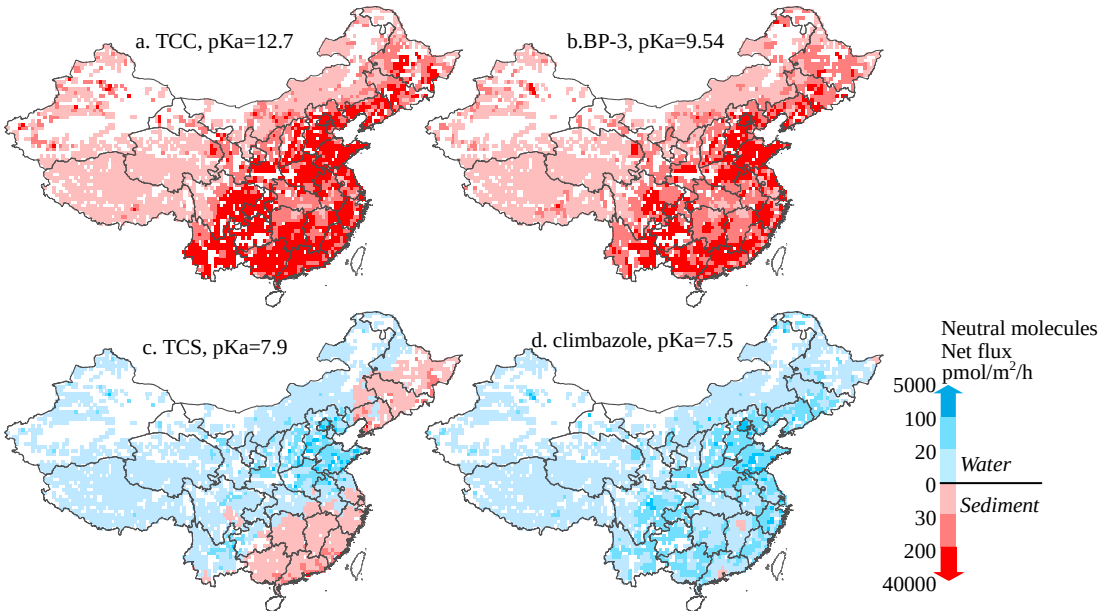

Figure 4 the net flux of neutral molecules of ionisable chemicals between freshwater and sediment compartments in the scenario that chemical is all released to water; blue indicates the net flux from sediment to freshwater and red is from water to sediment

As a result of constant emission to freshwater, the total molecules (neutral plus ionic forms) of all six chemicals and ionic molecules of the four ionisable chemicals are predicted to be transported from freshwater to sediment across China at steady state (Figure S13). However, the regionally varied main transport direction of neutral molecules (the main toxic form) of TCS and climbazole (Figure 4) demonstrates that the fate of ionisable chemicals is sensitive to small changes in environmental pH if their pKa values are within the range of ambient pH. The neutral molecules of TCS and climbazole are mainly transported from freshwater to sediment in red areas but from sediment to freshwater in blue areas. In red areas (lower water pH), chemicals are mostly present in the neutral form in freshwater after being released and so are transported mainly from water to sediment. In blue areas (higher water pH), a higher proportion of molecules are in the ionic form in freshwater but become neutral after partitioning to sediment (pH 0.6 lower than that in water), so neutral molecules partition back to freshwater. The water pH ranges of red areas are 6.8-7.8 for TCS and 6.8-7.2 for climbazole (Figure 4c-d). However, the sediment pH assumption is only one scenario, so there might be regional uncertainty due to the possibly different sediment pH values in the actual Chinese environment. Sediment can therefore act as either a receiving compartment or a source for neutral/toxic molecules of ionisable chemicals. BP-3 and TCC are mainly present in their neutral form in the Chinese environment, unless the region is polluted resulting in an abnormally high pH, so neutral molecules are mainly transported from freshwater to sediment across China.

Not all of these 'down-the-drain' chemicals emitted to water primarily remain or degrade in the aquatic environment. At the national scale, agricultural soil is also predicted to be an important compartment at steady state for ionisable chemicals with relatively low pKa and logKow values. However, the origin of the chemical loading is assumed to originate from water irrigation as land application of sewage sludge or wastewater released directly to soil is currently not considered. For example, TCS (54% in soil and 41% in freshwater sediment, respectively), climbazole (63% in soil, 13% in freshwater sediment and 18% in freshwater) and BP-3 (54% in soil, 21% in freshwater sediment and 19% in freshwater) are all predicted to be transported to soil via irrigation (Figure S11, Table S8 and details see Supporting information). These chemicals have either relatively low logKow (BP-3) or low pKa (TCS) or both (climbazole), so a higher proportion will be present in freshwaters rather than in sediments when continuously released compared to chemicals with high logKow and pKa (Figure 1). They can subsequently be transported to agricultural soil by freshwater irrigation and converted to neutral forms (BP-3 is already neutral) in most regions in China with ca. 85% regions of soil pH < 7.5. The neutral molecules tend to adhere to soils. Climbazole has both lower pKa and logKow, so it is modelled to have the highest proportion in soils among the three. However, it should be noted that despite representing an important environmental compartment that chemicals tend to distribute in, soil concentrations of these chemicals are low as stated above, and are far below the terrestrial toxicity threshold;[48, 49] Irrigation will probably not be the main source of such chemicals to soil regionally if sludge amendment[50] or direct re-use of wastewater to soil is routinely used.

The other three neutral (TCC is almost neutral) hydrophobic chemicals are modelled to partition more to sediment after release, so only a limited proportion of chemicals will be transported to soil by freshwater irrigation, i.e. TCC (85% in freshwater sediment, 8% in agricultural soil and 1.7% in freshwater), OC (91% in freshwater sediment, 3% in soil, 1.7% in freshwater) and OMC (77% in freshwater sediment, 12% in agricultural soil, 7% in freshwater) (Figure S11). The chemical distribution in different media can vary regionally, as shown in Figure S12. Regional uncertainty should be noted owing to the assumptions on agricultural irrigation with constant amount of freshwater per area in this model. In reality, agricultural production may vary in different regions, e.g. rice and wheat, which will require significantly different amounts of irrigation water per area; and the source of irrigation water may not only come from the local surface water in some regions but from other regions/grid cells. However, no monitoring data is available to explore the validity of this prediction. More discussions on vegetation can be found in Supporting Information.

This is a first study accounting for environmental fate of ionisable chemicals at the national scale for China. The findings that TCS and climbazole mainly distribute in soil at steady state

(Figure S11) contrast with conclusions by Zhang et al. that the greatest amount of chemical is predicted to be in sediment for climbazole (83.7%)[46] and TCS (96.7%)[45]. It is believed that conclusions on environmental fate of these chemicals are more refined in this study, because in Zhang's study (1) only sewage irrigation was considered (no freshwater used), which provides insufficient water supply for agricultural irrigation requirements, so the chemical transfer to soil is likely to be underestimated; and (2) the two chemicals were modelled in their neutral form only, which would probably overestimate the ratio of chemicals in sediment to those in water, especially for TCS with a higher logKow than climbazole.,If modelling TCS as a neutral chemical by SESAMe v3.3, it appears that the predicted nationally averaged concentration in sediment is approximately twice as high as that predicetd by modelling it as an acid, So in this study, although sewage irrigation hasn't been considered, freshwater irrigation, albeit with diluted chemical concentrations compared to wastewater, is predicted to be an important source of the two chemicals to soil. This conclusion is probably applicable to many other down-the-drain chemicals with low pKa or logKow values.

Accounting for ionisable chemicals in environmental risk assessment

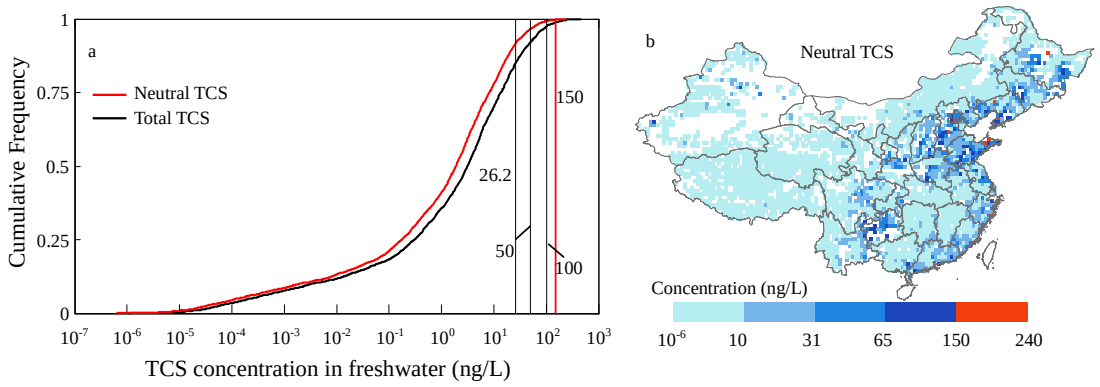

Figure 5 a, cumulative frequency of total and neutral TCS concentration in freshwater and the comparison with PNEC or other guideline values reported for water shown as vertical lines (the red vertical line representing 150 is $PNEC_n$); b, concentration of neutral TCS in freshwater across China.

An illustrative pH dependent environmental risk assessment has been conducted on TCS by comparing its $PNEC_n$ (150 ng/L) with both the PEC and the PEC_n produced by SESAMe v3.3 (Figure 5a). It was estimated that limited freshwater areas (0.03%, 55 km^2) in mainland China have PEC_n values exceeding 150 ng/L. These areas are mainly in NCP, Liaodong Peninsula and Shandong Peninsula, as shown in red in Figure 5b, which requires further investigation by researchers to ascertain actual environmental risks posed by TCS and its relative contribution versus other wastewater constituents (e.g. pharmaceuticals, substances released with industrial wastewater and pesticides etc.). The blue areas in Figure 5b are probably of

lower risk than the red areas on average (more discussions see Supporting Information). However, the different vertical lines in Figure 5a indicate the significant deviation of environmental risk assessment if a distinct threshold is chosen; and if comparing PEC with the threshold, the areas at risk will probably be overestimated.. The same method can be applied to sediments and soils for other ionisable chemicals.

Potential application of SESAMe v3.3 in chemical management in China

The use of these case study chemicals is illustrative and a previous model version has also been successfully applied on benzo[a]pyrene, with a greater focus on atmospheric emissions.[10] The illustrations show that SESAMe v3.3 can be a potential tool linking emissions, exposure concentrations in the environment with toxicity data. This can provide chemical prioritization and screening level assessment with spatial information, which could potentially resolve the issues stated at the beginning in the introduction and provide a guide to identify relatively high risk regions for monitoring campaigns and a refined risk assessment, which can support chemical management in China.

Why SESAMe v3.3 Firstly, as a multimedia fate model, the outputs can be easily interpreted by decision makers, which has been previously argued to be an advantage compared to more sophisticated models such as chemical transport models.[51] Secondly, SESAMe v3.3 can predict concentrations in multiple media for a broad range of chemicals including ionisables, which is competitive for developing an effective chemical management strategy with consideration of different exposure pathway to the environment or humans. It surpasses models which only predict concentrations within a single environmental compartment (e.g. atmospheric models and water quality models etc.). Besides, for chemicals mainly released to water, water quality models (such as GREAT-ER[52] etc.) currently cannot model at the national scale owing to the high requirements for hydrological parameters, but reversely SESAMe v3.3 can be used. Very few national scale studies using multimedia models for China have been implemented or published to date. As discussed above, the river basin based multimedia models by Zhang et al. for national modelling of pharmaceuticals and PCPs for China[45, 46, 53, 54] are fugacity models, which will probably result in higher uncertainty in concentration and fate estimations for ionisable chemicals.

Role in national water quality management Wu et al. (2010) has indicated that China should make its own national water quality criteria (WQC) system, rather than take the WQC from developed countries directly, as China has different eco-environmental systems/structures and priority pollutants as compared with other countries[55]. Besides, the priority pollutants probably vary regionally within the country, due to the diverse environmental conditions[11] and unbalanced economic development across the country.

Currently approaches to water quality management in China are usually adopted at the river basin or provincial level by different institutions, which may result in incompatible approaches between regions. National estimates of chemicals in aquatic systems by SESAMe v3.3 could provide an overall perspective for a national strategy with a unified method. Before this, BasinBox has been an example of multimedia fate models being developed for evaluating chemical risks in river basins for EU.[56]

Role in new chemical registration management Because quantitative risk assessment is required for new chemicals registration in China,[9] SESAMe v3.3 could also be used for preliminary risk estimation before a chemical is allowed to enter the Chinese market. For registration purposes and definitive risk assessments, data on the mass or volume of chemicals to be introduced to the market are required which can be used for the estimation of emissions, otherwise, OECD emission scenario documents[57] can be utilized to explore chemical emissions for a screening level assessment. A national strategy for estimating chemical usage in the country is important and needs be established. Care should be taken when using predictive tools to estimate physico-chemical properties and toxicity data for all chemical registrations. In particular, the use of mathematical estimations by models such as EPI Suite[58] should be carefully interpreted for ionisable chemicals[59] but has been widely used by researchers, which may cause higher uncertainties. In particular, the pH conditions for toxicity data should be reported for ionisable chemicals to properly interpret study results for use in risk assessment.

Supporting information

Additional information on description of model features, methods, input parameters, the literature for measured data and output figures are in the Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at http://pubs.acs.org/.

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Supporting information

A multimedia fate model to support chemical management in China: a case study for selected trace organics

Ying Zhu[1], Oliver R. Price[2]*, John Kilgallon[2], Cecilie Rendal[2], Shu Tao[3], Kevin C. Jones[1], and Andrew J. Sweetman[1]*

[1]Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, United Kingdom

[2]Safety and Environmental Assurance Centre, Unilever, Sharnbrook MK44 1LQ, United Kingdom

[3]Laboratory for Earth Surface Processes, College of Urban and Environmental Sciences, Peking University, Beijing 100871, China

*Corresponding author email:

Andrew J. Sweetman, a.sweetman@lancaster.ac.uk

Oliver R. Price, Oliver.Price@unilever.com

30 pages; 13 figures; 8 tables; 9 equations

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Figure S11 nationally averaged chemical distribution in different media at steady state in the scenario that chemicals are only released to freshwater; the percentage was calculated by the amount of chemical in the bulk of environmental media at steady state

Figure S12 regional TCS distribution in different media around Yangtze River Delta at steady state in the scenario that chemicals are only released to freshwater; the percentage of TCS in pie charts was calculated by the amount of chemical in the bulk of environmental media

Figure S13 Net flux of total molecules of six chemicals (A) and ionic molecules of ionisable chemicals (B) between freshwater and sediment in the scenario that the chemical is released to water.

Model feature, environmental and chemical parameters

Model feature SESAMe v3.3 presented in this study is a further developed version based on a previous version SESAMe v3.0 published by Zhu et al. (2015).[1] The model includes air, freshwater and sediment, sea water and sediment, natural soil, agricultural soil, urban soil, natural vegetation and agricultural vegetation compartments. The model structure and input environmental database are almost the same for the two versions, except for the update with spatially varied freshwater pH and sediment pH across China in SESAMe v3.3. It is a regional multimedia chemical fate model with environmental database for 5468 adjacent but independent grid cells (50×50 km^2, regional scale) covering the mainland China (exclusive of Hainan and Taiwan). So the model does not predict the directionally advective transport between regional grid cells. To take into account the input and effect from surrounding regions, a larger scale, continental scale (150×150 km^2), has been developed, which is composed of 8 adjacent 50×50 km^2 grid cells The continental scale is surrounding and interlinked to regional scale grid cell by advective flow in air and water. Such structure is shown in Figure S1 in a previous paper by Zhu et al.[1]

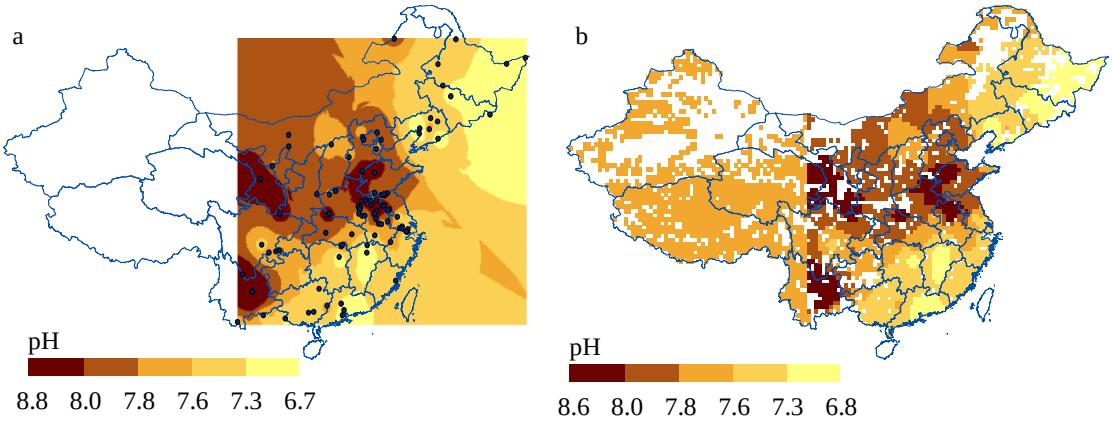

Figure S1 spatial distribution of freshwater pH in China

The formulas for modelling the concentration and fate of ionisable chemicals are the same as the first version of SESAMe model published by Zhu et al. (2014),[2] which have essentially referred to the equations in MAMI III model.[3, 4] For vegetation compartment, which is not considered in MAMI III model, the calculation has been shown in the Supporting Information (SI) of the paper on the first version of the model.[2] It has referred to the relevant calculations for vegetation compartment in Simplebox 3.24a.[5] The vegetation compartment has been considered as a homogenous compartment without separating the different parts of vegetation, e.g. the root and leaf etc. This allows a rough estimation of spatial distribution of chemical levels in vegetation across China and the main source of chemical to vegetation, e.g. from air or soil, which however are not the main topic of this study but worth mentioning.

logD is the log-transformed octanol-water partition coefficient for ionisable chemicals. D has been calculated in the model as below:[3]

$$D = f_{n,pH7} \times K_{ow,n} + (1 - f_{n,pH7}) \times K_{ow,ion} \quad (1)$$

$$K_{ow,ion} = 10^{logK_{ow,n}-3.5} \quad (2)$$

Notes:

$f_{n,pH7}$: fraction of neutral form of chemicals when solution pH=7 (-);

$K_{ow,n}$: i.e.K_{ow}, the octanol-water partition coefficient of a chemical for the neutral form (-);

$K_{ow,ion}$: the K_{ow} for the ionic form of chemicals (-).

This also has been used in logD calculation in Figure 1.

Kaw (Henry's law constant) can be also pH dependent for ionisable chemicals. However, as (1) the pH dependent Kaw is not calculated and used in SESAMe v3.3 model and (2) it is not significant for target chemicals in this study which have very low concentrations in air either, it is not the point being discussed in this study and, therefore, not shown in Figure 1 with y-direction error bars. In SESAMe v3.3, Kaw (temperature corrected) for neutral molecules has been used for calculating the partitioning of neutral species between air and water with fraction of neutral molecules in water, as only neutral molecules in water can volatile to air. The formulas relevant to diffusive transport flow of chemicals between air and water have referred to MAMI III model and are below:[3]

Water-air mass transport coefficient ($MTC_{water-air}$):

$$MTC_{water-air} = \frac{1}{\frac{f_{dissolved,n}}{MTC_{water-air,w}} + \frac{1}{K_{aw} \times MTC_{air}}} \quad (3)$$

$$MTC_{water-air,w} = 0.01 \times (0.0004 + 0.00004 \times windspeed^2) \times (32/MW)^{0.25} \quad (4)$$

$$MTC_{air} = 0.001 \times (0.3 + 0.2 \times windspeed) \times (18/MW)^{0.335} \quad (5)$$

Gas absorption flow from air to water:

$$GasAbs = f_{aerosolw,n} \times MTC_{water-air} \quad (6)$$

Volatilization flow from water to air:

$$\text{Volatilization} = f_{dissolved,n} \times MTC_{water-air} \quad (7)$$

$f_{dissolved,n}$: fraction of neutral molecules of chemicals dissolved in water phase (-);

$MTC_{water-air,w}$: water side mass transport coefficient between air and water (m/s);

MTC_{air}: air side mass transport coefficient (m/s);

MW: molecular weight (g/mol);

K_{aw}: dimensionless in SESAMe v3.3;

$f_{aerosolw,n}$: fraction of neutral molecules in aerosol water (-);

Freshwater pH generation To aim the ionisable chemicals in this study, spatially varied freshwater pH has been produced. Weekly reported freshwater pH (average taken from gauging data measured every four hours during the week) from 99 gauging stations (located as shown in Figure S1a) in China has been collected from the database of Ministry of Environmental Protection (MEP) of China for the whole year 2012.[6] The annual average freshwater pH has been calculated for each gauging site. A continuous surface water pH layer (1 km^2) has been generated by interpolating these point values by inverse distance weighting (IDW) interpolation method in ArcGIS 10.2.2. The freshwater pH layer can only cover the middle and the east of China (Figure S1a), as the water gauging stations all distribute in these areas. The 1-km^2 freshwater pH has been aggregated to 50×50 km^2 grid with a range of 6.8-8.6 and median 7.8. The median pH has been taken to complement the missing freshwater pH for western China (Figure S1b). The white area in Figure S1b indicates no surface water there.

Soil pH distribution Figure S2 shows the spatial distribution of pH for agricultural soil across China. The white area indicates no agricultural soil there.

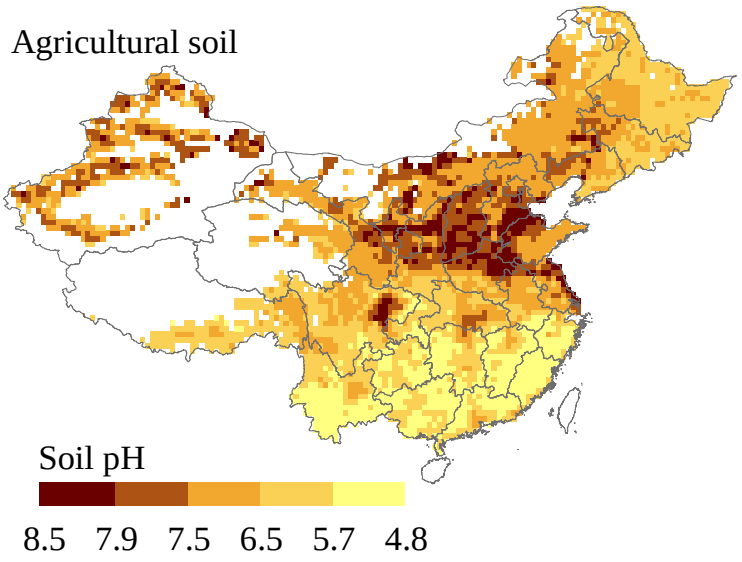

Figure S2 spatial distribution of agricultural soil pH in China

Chemical properties chemical properties related to partitioning were mostly measured values from experimental studies collected from literature.

Table S1 physico-chemical properties of the six chemicals

	Chemical	Molecular weight ($g \cdot mol^{-1}$)	Vapor pressure at 25 ˚C (Pa)	Water solubility at 25 ˚C ($g \cdot m^{-3}$)	Log K_{OW} (-)	pKa (-)	Half-life in air (hr)	Half-life in water (hr)	Half-life in sediment (hr)	Half-life in soil (hr)
Antibacterial	Triclosan (TCS)	289.54	6.9E-4[a]	8.8[b]*	4.8[b]	7.9[c]	15.9[d]	36[a]	12960[e]	2880[e]
	Triclocarban (TCC)	315.58	4.6E-11[i]	0.0237[b]	5.8[b]	12.7[c]	12.1[d]	1440[e]	12960[e]	2880[e]
	Climbazole	292.8	9.6E-4[b]	58[b]	3.83[b]	7.5[f]	4.87[g]	1440[g]	13000[g]	2880[g]
UV filters	Benzophenone-3 (BP-3)	228.24	1.1E-3[b]	6[b]	3.6[b]	9.54[h]	1.28[g]	900[g]	8100[g]	1800[g]
	Octocrylene (OC)	361.48	4.2E-7[b]	3.8E-3[g]	6.9[g]	neutral	7.9[g]	360[g]	3240[g]	720[g]
	octyl methoxycinnamate (OMC)	290.4	9.9E-3[g]	0.1548[g]	5.8[g]	neutral	4.17[g]	360[g]	3240[g]	720[g]

Notes: MW, molecular weight; VP, vapour pressure; WS, water solubility.

* extrapolated by ECHA experimental data for solubility at 25 ℃ (3.6 mg/L at 10 ℃; 6.5 mg/L at 20 ℃; 10.8 mg/L at 30 ℃).[7]

a, McMahon et al., 2008;[8]

b, ECHA registered chemical database;[7] c, Loftsson et al., 2005;[9]

d, Zhao et al., 2013;[10]

e, Halden et al., 2005;[11]

f, Chen et al., 2013;[12]

g, EPI Suite;[13]

h, Castro et al., 2003;[14]

i, US EPA, *Initial Risk-Based Prioritization of* HPV chemicals.[15]

Methods of emission estimation

Chemical inclusion levels Inclusion levels of chemicals in products are shown in Table S2.

Table S2 Inclusion levels of chemicals in different sub-categories of products

Chemicals	Categories	Sub-categories	Inclusion level
TCS	Oral Hygiene		0.30%[16]
	Soap & Bath Products		
	Dishwashing Products		
	Fabric Care		
	Skincare		
	Hair Products		
	Diapers & Feminine Hygiene		
	Deodorants		
	Hard Surface Care		
	Toilet Care		
	Fragrances		
	Shaving & Depilatories		
TCC	Soap & Bath Products		0.30%[16]
	Dishwashing Products		
	Fabric Care		
	Hair Products		
	Diapers & Feminine Hygiene		
	Deodorants		
	Hard Surface Care		
	Toilet Care		
	Fragrances		
	Shaving & Depilatories		
Climbazole	Deodorants		0.50%[17]
	Feminine Hygiene Products		2.00%[17]
	Hair products	Conditioner	0.50%[17]
		Hair Styling	0.50%[17]
		Hair Treatments	0.50%[17]
		Shampoo	1.00%[18]
	Skincare products (body, neck and face)	Body Care	0.50%[17]
		Face/Neck Care	0.50%[17]
	Soap & Bath Products	Bar Soap	2.00%[19]
		Shower Products	2.00%[19]
OMC	Deodorants		4.24%[b]
	Dishwashing-hand		4.24%[b]
	Hair products	Conditioner	3.00%[18]
		Hair Styling	3.00%[18]
		Hair Treatments	3.00%[18]
		Shampoo	3.00%[18]
	Shaving & Depilatories	Depilatory	2.94%[20]

		Products	
		Shaving Preparations	2.94%[20]
	Skincare	Body Care	7.14%[18]
		Face/Neck Care	5.58%[a]
		Hand/Nail Care	7.38% [a]
		Lip Care	3.36%[20]
		Sun - After Sun	4.24%[b]
		Sun - Sun/Sunbed Exposure	6.99% [a]
	Soap & Bath Products	Bar Soap	4.24% [b]
		Liquid Soap	4.24% [b]
		Shower Products	4.24% [b]
OC	Deodorants		7.00% [c]
	Hair products	Conditioner	10.00%[18]
		Hair Styling	10.00%[18]
		Hair Treatments	10.00%[18]
		Shampoo	10.00%[18]
	Skincare	Body Care	2.00%[18]
		Face/Neck Care	3.88% [a]
		Hand/Nail Care	2.76% [a]
		Lip Care	7.40% [a]
		Sun - After Sun	7.00% [c]
		Sun - Sun/Sunbed Exposure	5.69% [a]
	Soap & Bath Products	Liquid Soap	7.00% [c]
		Shower Products	7.00% [c]
BP-3	Deodorants		4.84%[d]
	Hair products	Conditioner	6.00%[18]
		Hair Styling	6.00%[18]
		Hair Treatments	6.00%[18]
		Shampoo	6.00%[18]
	Shaving & Depilatories		4.84% [d]
	Skincare	Body Care	3.50%[18]
		Face/Neck Care	4.64% [a]
		Hand/Nail Care	3.00%[18]
		Lip Care	3.62% [a]
		Sun - After Sun	4.84% [d]
		Sun - Sun/Sunbed Exposure	5.40% [18]
	Soap & Bath Products	Bar Soap	4.84% [d]
		Liquid Soap	4.84% [d]
		Shower Products	4.84% [d]

Notes: a, mean value of the inclusion level reported by Manová E et al.[20] and in Mintel database[18];
b, mean value of inclusion levels of OMC in the other products under the same category;
c, mean value of inclusion levels of OC in the other products under the same category;
d, mean value of inclusion levels of BP-3 in the other products under the same category.

Usage The usage (tonnes) of each chemical in products being sold in Chinese market for year 2012 has been calculated as equation (8).

$$\text{Usage} = \sum_i F_i \times T_i \times I_i \quad (8)$$

where i represents (sub)category i; F_i, T_i, I_i are respectively the fraction of products containing a specific chemical sold in Chinese market, the total tonnage of products sold in Chinese market (tonnes) and the inclusion level of the chemical in (sub)category i.

Percentage of wastewater connected to WWTPs Population connected to WWTPs has been estimated as the province-level domestic consumption wastewater discharge (National Bureau of Statistics (NBS) of China, 2009)[21] divided by the daily per capita domestic water use for that province. And then the percentage of the provincial population connected to WWTPs has been calculated and assigned to each county within that province. Due to the lack of specific data from the NBS of China, assumptions have been made such that urban and rural per capita water use is the same; and the urban population has been assigned WWTP connectivity before any rural population. If the estimated total population connected to WWTP exceeds the urban population in the same province, the remaining population have been considered as rural population and the percentage of rural population connected to WWTPs has been assigned to each county in that province. Province-level values used to calculate the population connected are included in Table S3.

Removal ratio of climbazole in WWTPs The predicted removal ratio of climbazole in WWTPs by SimpleTreat 3.2[22] is 12%, which is out of the measured range (18 - 67%) from the literature. Climbazole is set as inherently not biodegradable in SimpleTreat model based on biodegradation tests with initial concentrations of 4 mg/L and 100 mg/L in water reported by European Chemical Agency (ECHA),[7] however its actual concentration in raw wastewater to WWTPs is normally much lower (e.g. 1.4 ug/L[23] in Germany or 0.6-1.0 ug/L[24] in Beijing). It is well documented that under ready test conditions the unrealistic high concentration of test material can cause toxicity in the system and underestimate the removal.[25] Therefore, 40% has been taken for climbazole as stated in the main paper.

Table S3. Table of province level information used to develop estimates of WWTP connectivity

Province	Population (10,000) (2008)[1]	Urban Population (10,000) (2008)[1]	Rural Population (10,000) (2008)[1]	Per Capita Water Use (L/day)[2]	Domestic Consumption Wastewater Discharge (m3/day)[3]	Total Population Connected (10,000) (2008)	Total Population Connected (%)	Urban WWTP Connectivity (%)	Rural WWTP Connectivity (%)
Anhui	6,135	2,485	3,650	123	2,785,288	2,271	37%	91%	0%
Beijing	1,695	1,439	256	252	2,873,753	1,139	67%	79%	0%
Chongqing	2,839	1,419	1,420	169	2,139,342	1,269	45%	89%	0%
Fujian	3,604	1,798	1,806	167	2,637,589	1,579	44%	88%	0%
Gansu	2,628	845	1,783	96	851,096	883	34%	100%	2%
Guangdong	9,544	6,048	3,496	259	12,713,370	4,905	51%	81%	0%
Guangxi	4,816	1,838	2,978	286	3,824,932	1,339	28%	73%	0%
Guizhou	3,793	1,104	2,689	117	1,210,164	1,038	27%	94%	0%
Hainan	854	410	444	202	827,315	409	48%	100%	0%
Hebei	6,989	2,928	4,061	92	3,110,274	3,381	48%	100%	11%
Heilongjiang	3,825	2,119	1,706	135	1,974,959	1,466	38%	69%	0%
Henan	9,429	3,397	6,032	102	4,823,260	4,747	50%	100%	22%
Hubei	5,711	2,581	3,130	148	4,525,671	3,056	54%	100%	15%
Hunan	6,380	2,689	3,691	194	4,328,521	2,233	35%	83%	0%
Inner Mongolia	2,414	1,248	1,166	167	1,130,247	675	28%	54%	0%
Jiangsu	7,677	4,169	3,509	177	6,841,151	3,861	50%	93%	0%
Jiangxi	4,400	1,820	2,580	146	1,924,055	1,316	30%	72%	0%
Jilin	2,734	1,455	1,279	133	1,902,137	1,427	52%	98%	0%
Liaoning	4,315	2,591	1,724	156	3,532,822	2,261	52%	87%	0%
Ningxia	618	278	340	73	479,452	659	100%	100%	100%

Qinghai	554	227	327	165	353,397	214	39%	94%	0%
Shaanxi	3,762	1,584	2,178	102	1,545,370	1,513	40%	96%	0%
Shandong	9,417	4,483	4,935	99	4,984,493	5,046	54%	100%	11%
Shanghai	1,888	1,673	215	327	4,983,014	1,524	81%	91%	0%
Shanxi	3,411	1,539	1,872	79	1,801,671	2,285	67%	100%	40%
Sichuan	8,138	3,044	5,094	116	4,209,397	3,625	45%	100%	11%
Tianjin	1,176	908	268	117	1,117,699	958	81%	100%	18%
Tibet	287	65	222	218	68,384	31	11%	48%	0%
Xinjiang	2,131	845	1,286	158	1,419,863	898	42%	100%	4%
Yunnan	4,543	1,499	3,044	135	1,393,671	1,032	23%	69%	0%
Zhejiang	5,120	2,949	2,171	195	4,106,548	2,101	41%	71%	0%
National	130,827	61,477	69,350	153	90,418,904	59,097	45%	89%	6%

[1] National Bureau of Statistics of China, 2009 (Table 3-4)[21]
[2] National Bureau of Statistics of China, 2009 (Table 11-18)[21]
[3] National Bureau of Statistics of China, 2009 (Table 11-19)[21]
Note: National values for water use and WWTP connectivity are population-weighted

Toxicity data calculation

Orvos et al.[26] has indicated in their article that the concentration of the neutral molecules of TCS for EC50 is relatively constant at four different pH levels, which has been obtained from an exposure testing to daphnia. Roberts et al.[27] has provided toxicity data of TCS at pH levels of 7, 8 and 8.5 as shown in Table S4, which has been obtained from algae exposure testing. It also demonstrates that for each toxicity level, the concentration of neutral forms is relatively constant under different pH levels as shown in Table S4.

Table S4 toxicity data of TCS and its neutral concentration at different pH levels (ug/L)

pH	NOEC	$NOEC_{\cdot n}$*	LOEC	$LOEC_{\cdot n}$*	EC_{10}	$EC_{10\cdot n}$*	EC_{20}	$EC_{20\cdot n}$*	EC_{50}	$EC_{50\cdot n}$*
8.5	25.3	5.1	4.3	0.9	36.5	7.3	65.1	13.1	175.1	35.2
8.0	3.43	1.5	6.0	2.6	5.0	2.2	18.6	8.2	175.9	77.9
7.0	3.92	3.5	1.1	1.0	3.7	3.3	6.4	5.7	16.8	14.9

Notes: $EC_{x.n}$, $NOEC_{.n}$ and $LOEC_{.n}$, the concentration of the neutral form of corresponding toxicity data

Emissions estimated

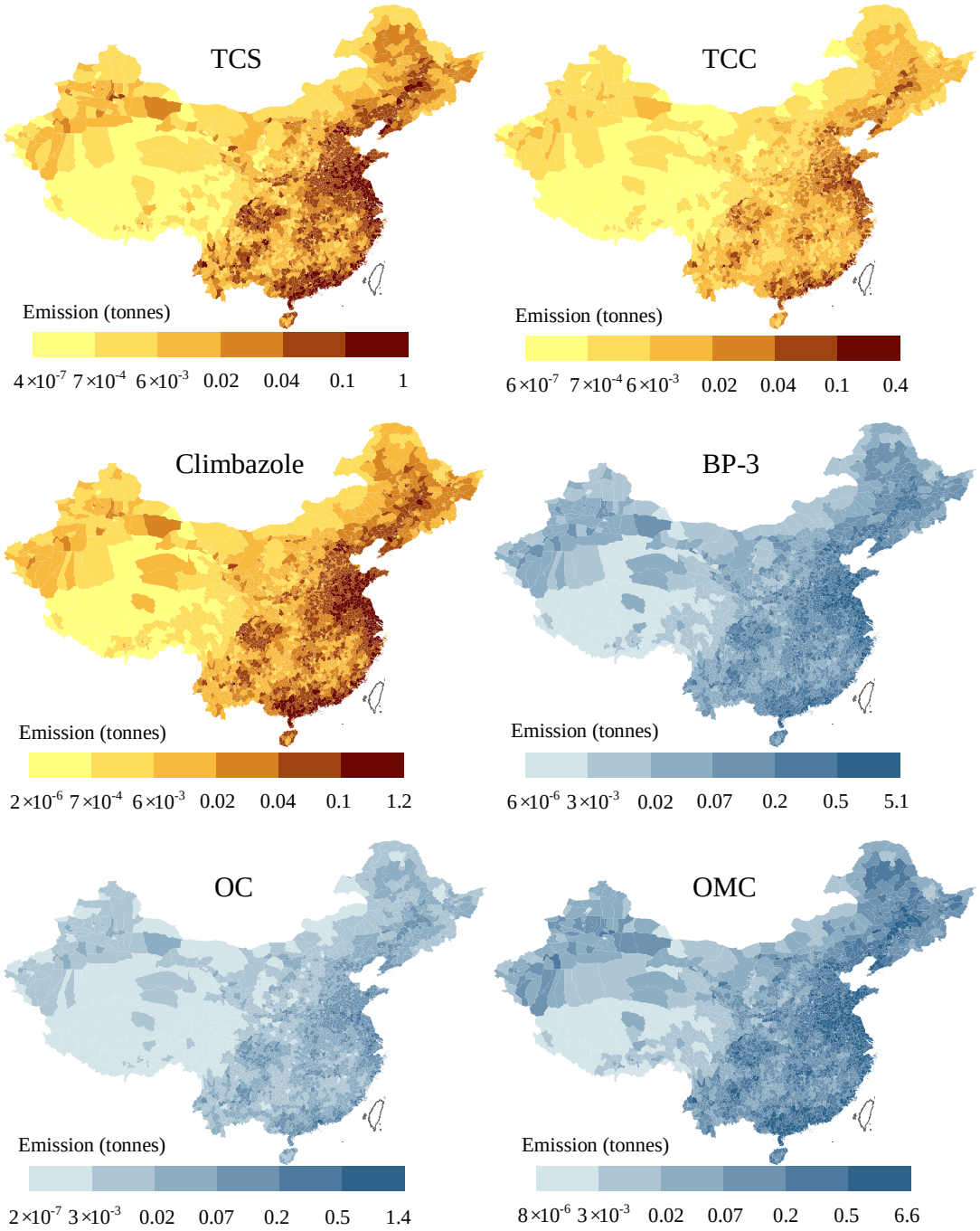

Figure S3 Emissions of three antibacterial agents (TCS, TCC and climbazole) and three UV-filters (BP-3, OC and OMC) by county

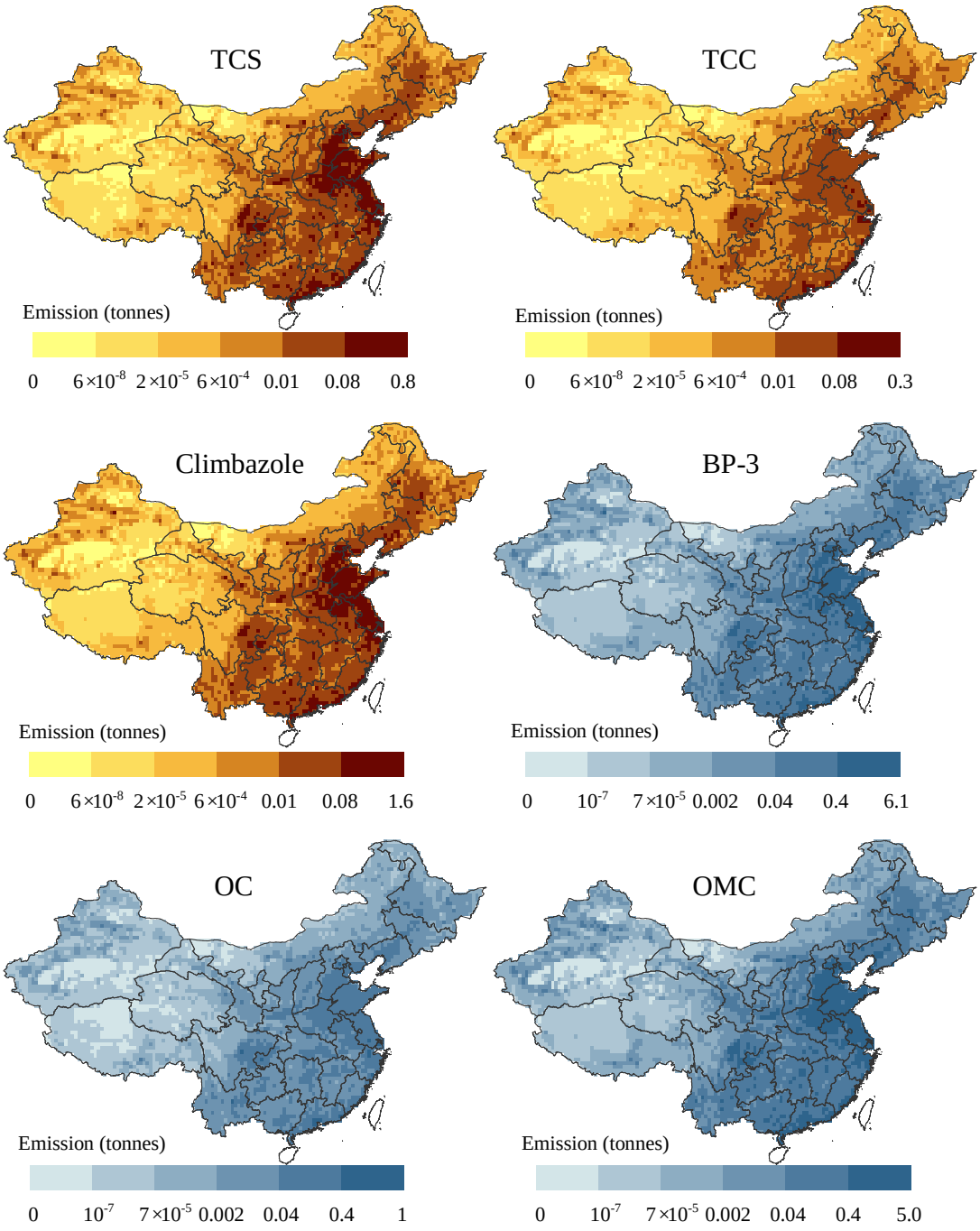

Figure S4 Emissions of three antibacterial agents (TCS, TCC and climbazole) and three UV-filters (BP-3, OC and OMC) by 50 ×50 km^2 grid

Model evaluation Methods

Method of sensitivity analysis (SCV) variability-based sensitivity coefficient has been used for the sensitivity analysis described in below equation.[28]

$$\mathrm{SCV} = \frac{\Delta CV_i^Y / CV_i^Y}{\Delta CV_i^X / CV_i^X} \quad (9)$$

where CV_i^X and CV_i^Y are respectively the coefficient of variance (CV) of values of the i^{th} input variable vector and the corresponding i^{th} predicted output. ΔCV_i^X and ΔCV_i^Y are their differences. The probability distribution of environmental parameters could be found in previous study by Zhu et al.[1] Parameters will be identified to be more influential to the model outputs if the corresponding SCV > 0.1.

Model outputs validation The sampling sites location of measurements from the literature is shown in Figure S5. The sampling size and related references are shown in Table S5.

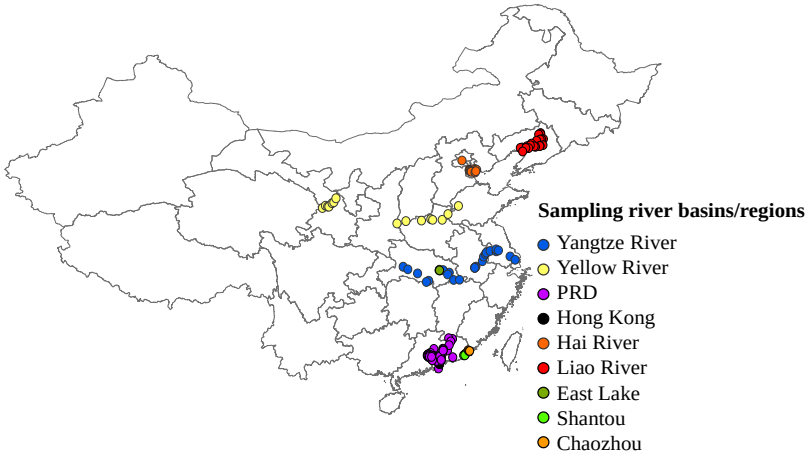

Figure S5 location of sampling sites of measurements

Table S5 Information for measured data collected from the literature

Chemical	Sampling sites	Sampling year	Sample size	reference
TCS TCC	Liao River	2007-2009	82	Zhao et al., 2013[10]
	Hai River	2007-2009	44	
	Yellow River	2007-2009	60	
	Dongjiang	2007-2009	119	
	Pear River	2007-2009	60	
Climbazole	Hai River	2009	13	Heeb et al., 2012[29]
	Dongjiang	2012	21	Chen et al., 2014[30]
	Yangtze River	2013	24	Zhang et al., 2015[31]
	Yangtze River	2009-2010	3	Qi et al., 2014[32]
BP-3	East lake	2013-2014	15	Wu et al., 2015[33]
	Shantou	2012	4	Tsui et al., 2014[34]
	Chaozhou	2012	3	Tsui et al., 2014[34]
	Hong Kong	2012	4	Tsui et al., 2014[34]
OC, OMC	Shantou	2012	4	Tsui et al., 2014[34]
	Chaozhou	2012	3	
	Hong Kong	2012	4	

Model evaluation results

Figure S6-S7 show the comparison between predictions and measurements.

The results of sensitivity analysis are shown in Table S6.

The probability distribution of the model output by Monte Carlo simulation is shown in Figure S8.

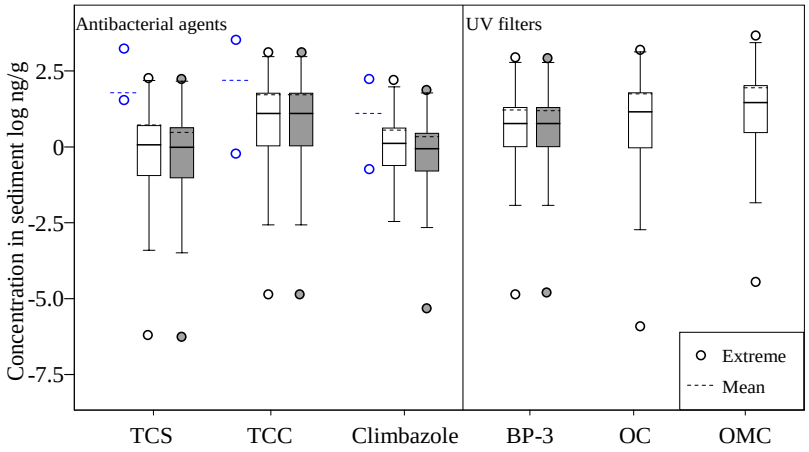

Figure S6 Boxplot (SPSS 18) of predicted total and neutral chemical concentration (predictions from all grid cells), and measurements in freshwater sediment (blue). White-box group indicates predicted total chemical concentrations (neutral plus ionic molecules); grey-box group indicates predicted neutral concentration; the horizontal solid line in the box is the median; the top and bottom of the box are respectively the 75th and 25th percentile; the top and bottom of the whisker are respectively the highest and lowest case within 1.5 times the interquartile range. Extreme circles are max/min values.

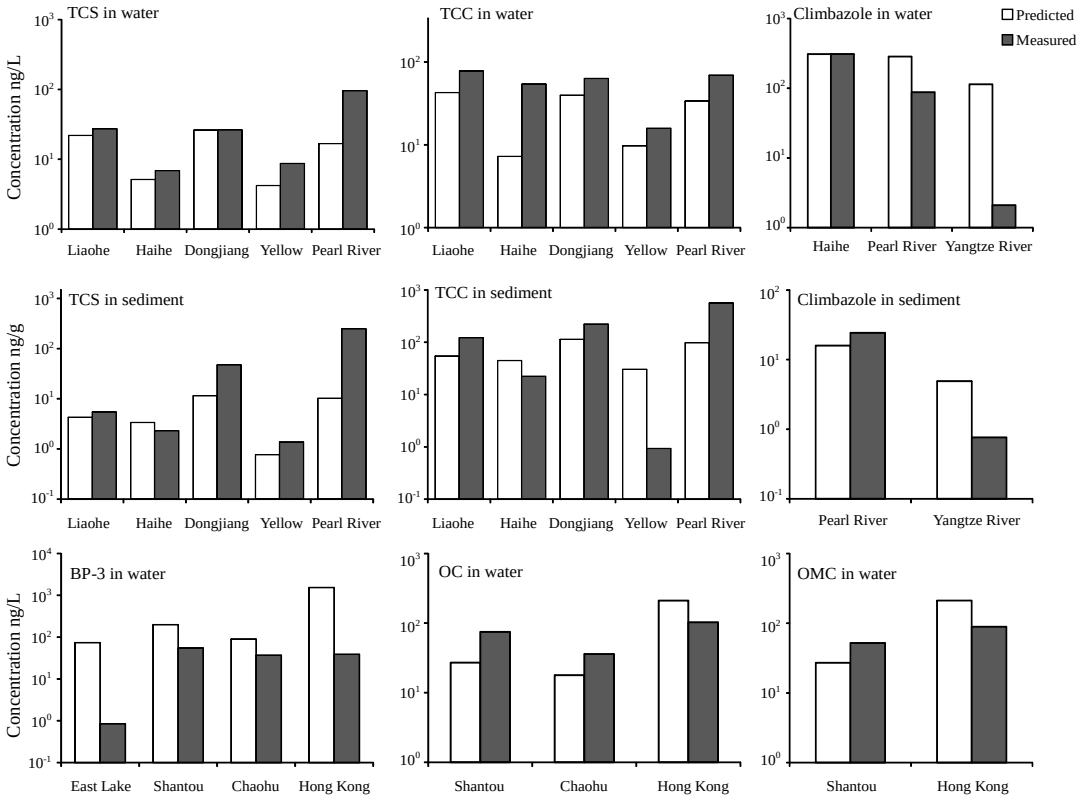

Figure S7 Comparison of predicted and measured concentrations in certain river/lake catchment

As the value for each sampling site is normally not provided but only mean is reported in the literature, the measured concentration in Figure S7 is the mean chemical concentration for individual river/lake catchment reported in the literature. If more than one monitoring study focus on the same river/lake catchment, measurements have been averaged for validation. The predicted concentration is the mean value of predicted concentrations for grid cells spatially covering the sampling sites for individual river/lake catchment in literature listed in Table S5 for each chemical.

Table S6 Index of SCV sensitivity analysis (>0.1)

	Triclosan		Triclocarban		Climbazole		Benzophenone-3		Octocrylene		Octyl methoxycinnamate	
Environmental parameters	Water	Sediment	Water	Sediment	Water	Sediment	Water	Sediment	Water	Sediment	Water	Sediment
Temperature	4.4	7.2	11.5	14.9	13.2	15.8	40.7	51.7	47.1	71.3	27.0	41.2
Wind speed	0.2	0.2			0.1		4.5	4.2			1.6	0.6
Precipitation		0.2						0.2				
Surface water depth	10.1	15.7	1.4	1.2	3.6	3.2	10.2	11.6	0.7	0.7	1.9	1.6
Water inflow	3.6	3.8	9.4	9.2	0.1	0.9	6.3	2.8	11.7	12.1	5.5	6.4
Water outflow	19.4	21.6	3.9	4.7	15.2	12.5	27.2	14.0	19.0	14.7	4.3	6.1
Runoff												
Soil water erosion rate												
Soil OC												
Soil Density	1.4	0.5	4.2	0.7	1.5	5.7	14.5	0.4	5.9	0.5	1.7	2.4
Sediment OC	2.3		0.4		0.4	1.0	4.8	1.3	0.2		0.5	0.7
Soil pH					0.2	0.2						
Freshwater pH	0.7	10.5			19.6	79.9	0.3	0.2				
Emission	118.1	210.5	4.9	4.7	3.0	4.7	1.1	1.5	2.7	2.6	6.1	6.1

The parameters with index higher than 0.1 are more influential than those with index lower than 0.1 (not shown in above table).

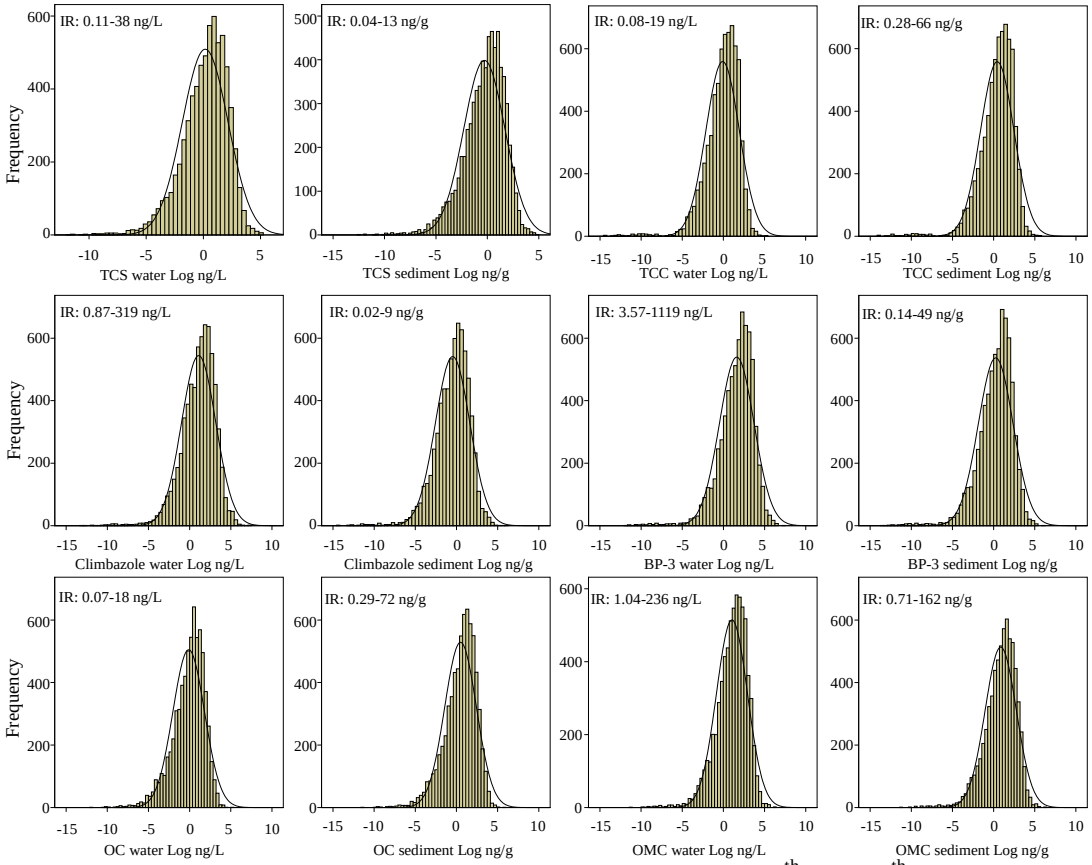

Figure S8 Lognormal distribution and interquartile range (IR, 25th and 75th percentiles) of predicted chemical concentration in freshwater and sediment by Monte Carlo simulation

Geographic distribution of six chemicals in freshwater and sediment across China

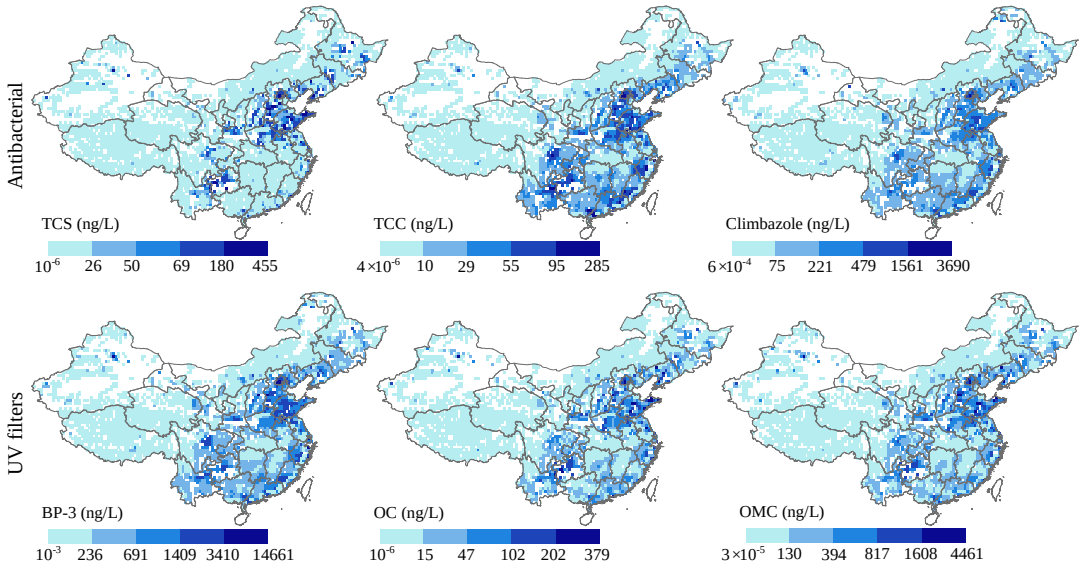

Figure S9 Predicted concentration for six chemicals in freshwater

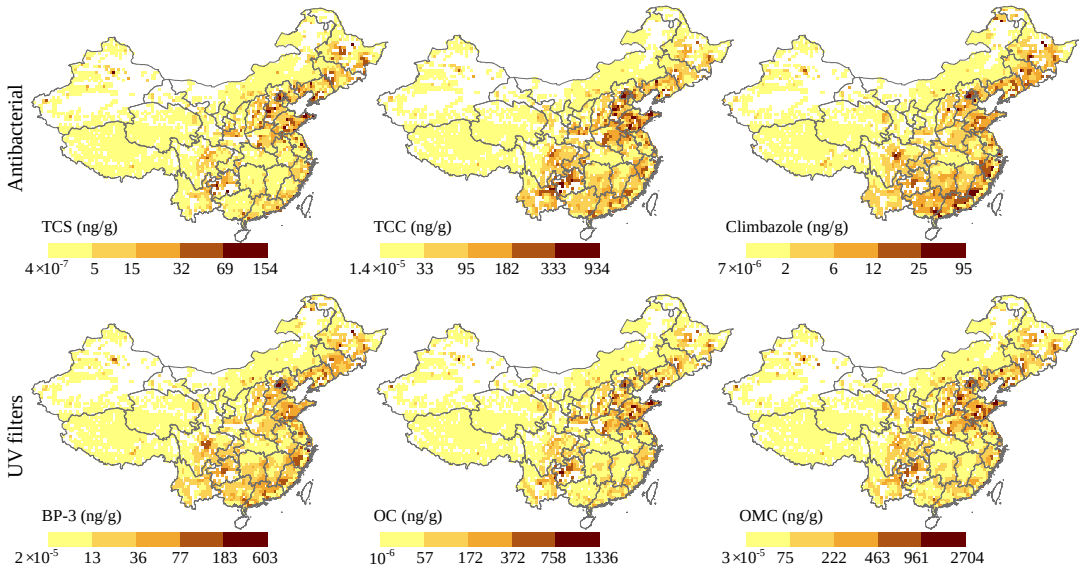

Figure S10 Predicted concentration for six chemicals in freshwater sediment

Range of concentration (5^{th} - 95^{th}, plus mean) at eastern coastal area is, in sea water 2×10^{-3} - 1.7 (0.4) ng/L for TCS, 0.02 - 11 (2.6) ng/L for TCC, 0.6 - 67 (19) ng/L for climbazole, 1 - 200 (55) ng/L for BP-3, 5×10^{-3} - 12 (2) ng/L for OC and 0.1 - 73 (17) ng/L for OMC; sea sediment, 6×10^{-4} - 0.6 (0.1) ng/g for TCS, 0.05 - 31 (6) ng/g for TCC, 0.02 - 3 (0.7) ng/g for climbazole, 0.05 - 9 (2) ng/g for BP-3, 0.01 - 25 (4) ng/g for OC and 0.03 - 22 (4) ng/g for OMC.

Table S7 Comparison of emission and predicted concentration range (Min - Max) in freshwater and sediment for TCS and climbazole between this study and Zheng et al.'s studies

TCS	Emission	Water concentration range	Sediment concentration range
This study	95 tonnes/yr	10^{-6} – 455 ng/L	4×10^{-7} – 154 ng/g
Zhang's study[35]	66.1 t/yr	0.0156 – 39.1 ng/L	0.00215 – 14.8 ng/g
climbazole	Emission	Water concentration range	Sediment concentration range
This study	107 tonnes/yr	6×10^{-4} – 3690 ng/L	7×10^{-6} – 95 ng/g
Zhang's study[31]	254 t/yr	0.2 - 367 ng/L	0.009 – 25.2 ng/g

As the concentration range reported in studies by Zhang et al.[31, 35] is Min - Max (minimum - maximum) instead of 5^{th} - 95^{th} percentiles, range of Min – Max has been taken for this study for comparison in Table S7.

Chemical partitioning in environmental media

Figure S11 and Figure S12 show respectively the nationally averaged chemical distribution of the six chemicals in different media and regional variation of TCS distribution in media around Yangtze River Delta as an example at steady state. It should be noted that they all show the percentage of total amount of a chemical in the bulk of environmental media but do not reflect the relationship of concentration levels of a chemical in different environmental media, e.g. concentrations of chemicals are relatively higher in freshwater and sediment but very low in soil including TCS, climbazole and BP-3 although the amount of the three chemicals distributing in soil is over 50% of all at steady state. And this is under the scenario that chemicals are only released to freshwater.

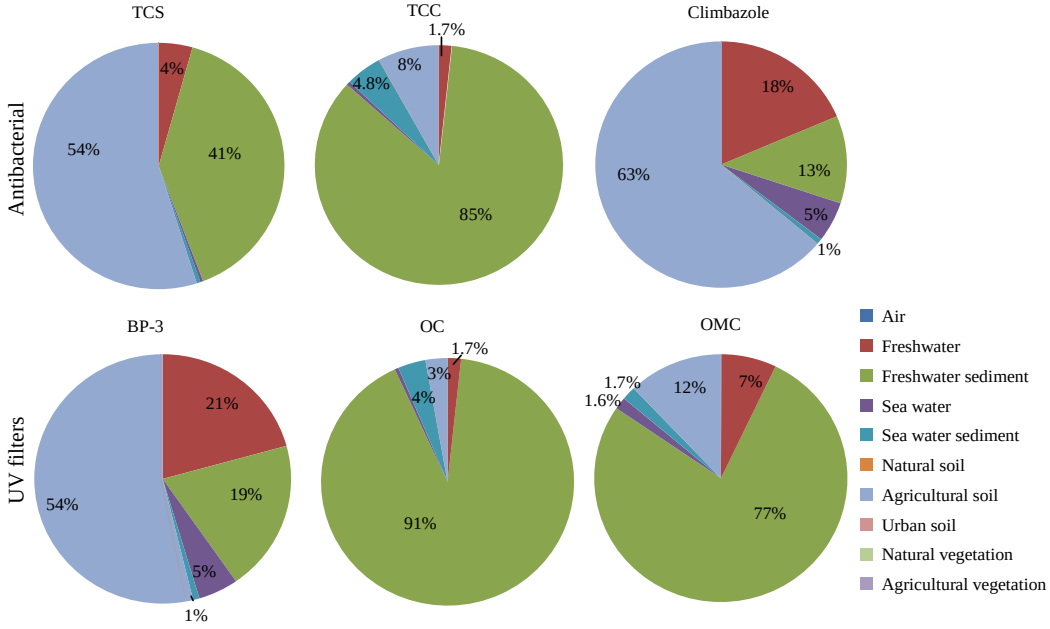

Figure S11 nationally averaged chemical distribution in different media at steady state in the scenario that chemicals are only released to freshwater; the percentage was calculated by the amount of chemical in the bulk of environmental media at steady state

Table S8 Flux (mean ± standard deviation) to agricultural soil from respectively freshwater irrigation, deposition and absorption from air and vegetation litter in national scale (Unit, mol/day/m^2)

Chemical	Irrigation	Deposition and absorption from air	Vegetation litter
TCS	$2.0\times10^{-11}\pm4.4\times10^{-11}$	$1.5\times10^{-15}\pm4.5\times10^{-15}$	$4.5\times10^{-18}\pm1.1\times10^{-17}$
climbazole	$1.1\times10^{-10}\pm1.8\times10^{-10}$	$7.9\times10^{-16}\pm4.5\times10^{-15}$	$1.7\times10^{-16}\pm3.6\times10^{-16}$
BP-3	$5.2\times10^{-10}\pm9.0\times10^{-10}$	$1.6\times10^{-15}\pm1.5\times10^{-14}$	$5.2\times10^{-16}\pm1.1\times10^{-15}$

As there is not any direct wastewater release to soil and sludge application to land, freshwater irrigation, deposition (wet + dry) and absorption from air and vegetation litter are three pathways that transport chemicals to agricultural soil. By comparing the fluxes

among different pathways in Table S8, freshwater irrigation is the main way that transports the three chemicals to agricultural soil.

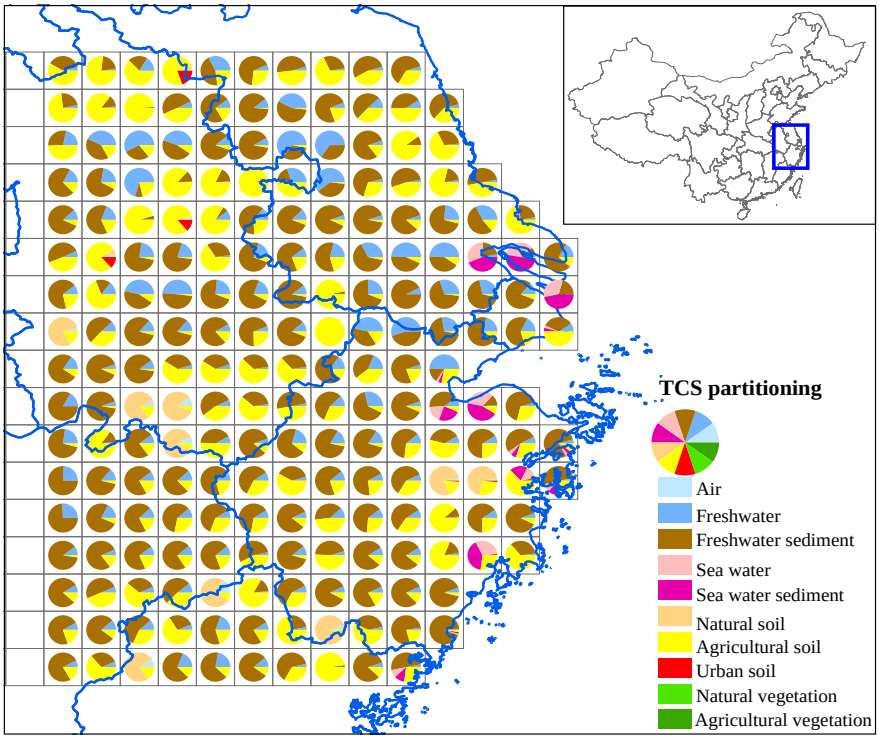

Figure S12 regional TCS distribution in different media around Yangtze River Delta at steady state in the scenario that chemicals are only released to freshwater; the percentage of TCS in pie charts was calculated by the amount of chemical in the bulk of environmental media

Level of chemicals in vegetation It is worth mentioning both the bulk amount and the concentration of chemicals in agricultural vegetation are very low. The percentage of the bulk amount of chemicals is close to zero as shown in Figure S11-S12. The median concentration of chemicals in agricultural vegetation is estimated at 2.3×10^{-9} (TCC) - 1.2×10^{-4} (BP-3) ng/g (dry weight, water contents in vegetation is assumed to be 95%), which is almost undetectable by devices for field samples.

There are evidences on plant uptake of home and personal care product ingredients from soils or under hydroponic conditions with relatively high concentrations in vegetation; however, these are mostly observed in laboratory or greenhouse experiments and concentrations in crops growing in realistic field conditions with biosolids application or treated wastewater irrigation are found very low.[36] This may result from various conditions including the chemical properties and system conditions, such as the medium the vegetation grows in, the pH in the growth medium and pH in cell etc.,[36] and perhaps needs to be studied further with more sophisticated model for vegetation or laboratory experiments.

Chemical transport between freshwater and sediment

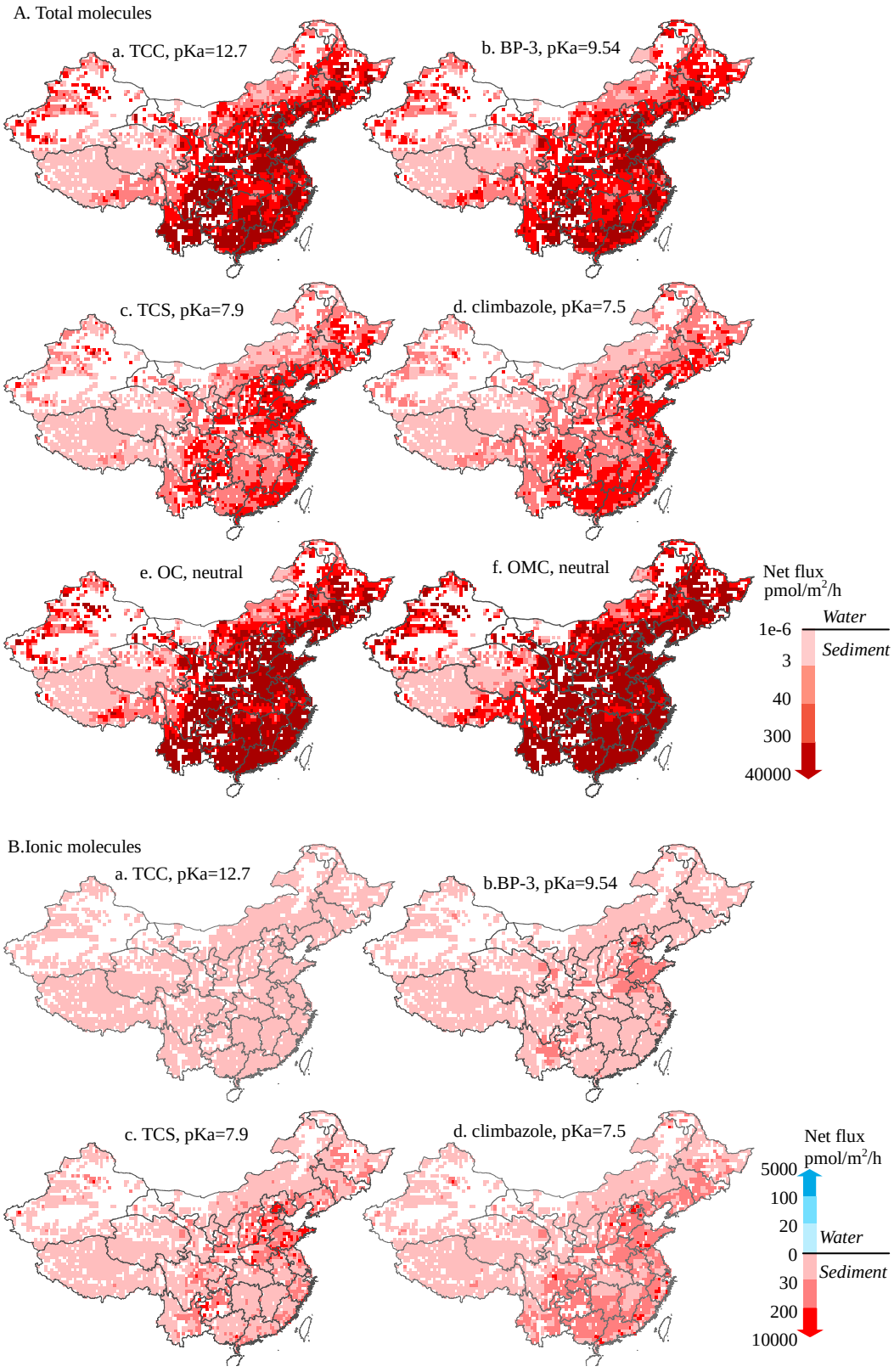

Figure S13 Net flux of total molecules of six chemicals (A) and ionic molecules of ionisable chemicals (B) between freshwater and sediment in the scenario that the chemical is all released to water.

Environmental risk assessment

It should be noted that due to the model limitation and uncertainty, SESEMe v3.3 can provide the information for identifying areas with higher or lower risk for a specific chemical, e.g. the red and blue areas in Figure 5b. However it does not mean all areas in blue are absolutely safe. SESAMe v3.3 can only provide average concentration within each grid cell but cannot identify the hotspots which are on or closely around the releasing sites. As a result of the reasonable deviation of model outputs, such hotspots possibly exist in blue areas in Figure 5b. Therefore, further risk assessment method may need to classify the blue area and identify areas with secondary level risk etc., which could be a further area for SESAMe v3.3 application.

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IV

Projected changes in environmental conditions, population, infrastructure and consumer spending on the use, emission and environmental distribution of selected organic chemicals in China

Ying Zhu[1], Oliver R. Price[2], John Kilgallon[2], Yi Qi[3], Shu Tao[4], Kevin C. Jones[1], and Andrew J. Sweetman[1*]

[1]Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, United Kingdom

[2]Safety and Environmental Assurance Centre, Unilever, Sharnbrook MK44 1LQ, United Kingdom

[3]Department of Urban Planning & Design, Nanjing University, Nanjing 210093, China

[4]Laboratory for Earth Surface Processes, College of Urban and Environmental Sciences, Peking University, Beijing 100871, China

*Corresponding author email:

Andrew J. Sweetman, a.sweetman@lancaster.ac.uk

Abstract

The freshwater concentration of selected organic chemicals used in consumer products, i.e. triclosan (TCS), triclocarban (TCC), climbazole, benzophenone-3 (BP-3), octocrylene (OC) and octyl methoxycinnamate (OMC), is predicted to be below the threshold in most regions across China for 2012, which will probably not raise the concern of environmental safety in China. However owing to the future expansion of demand on consumer products in Chinese market as a result of population change and economic growth, the increasing use of chemicals may lead to higher emission to aquatic system; meanwhile, the development of infrastructure and change of river discharge flow under a global warming scenario may decrease the emission and ultimately the environmental concentration. Therefore, a scenario for 2030 has been projected with considering these variables in this study for estimating the use, emission and environmental concentration of these chemicals across China. The use of the six chemicals in 2030 all increase and (except for TCC) is almost twice of that in 2012, due to economic growth. As a result of WWTPs construction, emissions in 2030 reduce for TCS, TCC and OC, increase less than twice for climbazole and BP-3 and do not have significant difference for OMC compared to that in 2012. SESAMe v3.3 predicts a lower concentration of all six chemicals in 2030 than that in 2012 with consideration of future change of river discharge flow. The most influential variable is concluded to be the construction of WWTPs

under the scenario in this study. This can probably be reference information for supporting the research, business sustainability and government decision-making.

Introduction

The occurrence of organic chemicals contained in consumer products, such as antibacterial agents, UV filters and preservative etc., have been more evident in water bodies and effluent of wastewater treatment plants (WWTPs) worldwide owing to the lower detection limit by the improvement of chemical analysis methods and technologies.[1, 2] Toxicity of many of these chemicals has been examined and observed in both aquatic and terrestrial organisms above certain thresholds in exposure testing.[3] To assess the environmental risk of such chemicals in the Chinese environment, the usage, emission and environmental concentration of example chemicals, i.e. triclosan (TCS), triclocarban (TCC), climbazole, benzophenone-3 (BP-3), octocrylene (OC) and octyl methoxycinnamate (OMC), have been estimated with a resolution of 50×50 km^2 across China for 2012 in our previous study[4] with a supporting model tool – SESAMe v3.3. Only a limited region was predicted with TCS water concentration exceeding the threshold, and generally, the predicted concentrations of all chemicals are lower than the exposure testing concentrations under which the toxicity to organisms can be observed.[5-8] Also, monitoring campaigns and other model predictions generally haven't found the environmental concentration above the level of concern.[9] However, despite the current relative safety, attention should be paid to these chemicals in the environment due to the rapid development of China.

OECD predicts that the per capita GDP will increase with rates ranging ca. 3.5-7% annually from 2012 to 2030, although growth will decelerate;[10] and considering the huge population and rapid urbanization which implies the improvement of life quality, the Chinese market has great potential for demand expansion for consumer products. This accordingly will lead to greater usage and potentially higher emission of organic chemicals contained in these products in future China. Meanwhile, the infrastructure in China has expanded quickly during 2004-2013, e.g. wastewater treatment plants (WWTPs).[11] The 12th five-year plan has made targets on WWTPs connectivity for regions with different administrative levels;[12] and by the end of 2015, new targets for years 2016-2020 will probably be released in the 13th five-year plan of China. Therefore, sewage treatment capacity and population connectivity to WWTPs will rise with the continual building of infrastructure. This reversely will decrease the emission of these chemicals to aquatic environment. In the meantime, the future river discharge with consideration of global climate change[13] may be influential to the aquatic concentration of chemicals.

It is of interest to investigate the influence of the expansion of products consumption, infrastructure and probable change of river dilution on the use, emission and environmental concentration and distribution of these chemicals in the future nominal year 2030 for China. There have not been studies, up to date as authors been aware of, on projection of consumer products consumption and relevant ingredient organic chemical usage for China and this will probably be the first study. A future scenario of infrastructure construction is developed to estimate the emission. With estimations of chemical environmental concentration by SESAMe v3.3 model, which has been proved to be a capable model on such chemicals, results may provide the supporting information for future business sustainability and efficiency of infrastructure construction for the government decision-making in China.

Methods and materials

Model and chemical selection

To investigate the change in 2030 compared to the base year 2012, the same six chemicals used in the previous study for 2012 were selected in this study for year 2030 and SESAMe v3.3 was applied for predicting the spatially explicit concentration of chemicals in mainly aquatic environment in China. The physicochemical properties and most environmental parameters were introduced in our previous study.[4] Only river discharge flow and surface water depth were considered to be changed in the model, as they are the main environmental properties that would affect the chemical concentration in aquatic system. A projection of river discharge flow for 2030 by GWAVA model was collected from WATCH database, which was predicted under the A1 IPCC climate scenario modelled by ECHAM5.[14] The corresponding surface water depth for 2030 was calculated by this discharge flow dataset with the method used in a previous study by Zhu et al.[15]

Future market size projection of consumer products

The future Chinese market size (the volume of products sold in a market) of consumer products which contain the six chemicals are vital for calculating the amount of future chemical usage. Mintel Global New Products database[16] provided the (sub-)categories of products containing each of the six chemicals during year 1996-2015 (29 subcategories belong to 12 categories , Table S1). Euromonitor database[17] provided the annual national market size of 29 subcategories individually during 2000-2019 for China. The history market size for year 2000-2014 was by market survey and that for year 2015-2019 was estimated by Euromonitor. It was assumed that the subcategories containing the chemicals would be the same for 2030. The national annual per capita GDP of China during year 2000-2030 was collected from OECD database.[10] Equations representing the regression of annual national per

capita GDP and market size during 2000-2019 were generated for individual subcategory (Figure S1). Most of them fit linear regression well, except for shampoo, bleach/disinfectant and all-purpose surface care product which fit logarithmic regression better and bar soap which fit 2nd order polynomial regression better. However for bar soap, as the market size will decrease dramatically to a minus value with per capita GDP increase till 2030 based on the regression assumption, the market size for year 2000 was assumed to be that for 2030 as a conservative estimation.

Future population

The population for year 2030 across China was predicted by Han et al.[18] with a resolution of 1 × 1 km^2. Despites the natural growth rates, the change of regional population would be relevant to the urbanization rates, e.g. migration of population to constructed area or more developed urban area from rural area. Therefore, the constructed area across China (resolution, 1 × 1 km^2) for 2030 was projected by Han et al. to predict the population. Grid cells with population greater than 5000 were identified as urban extent[19] and the others were rural population in ArcGIS 10.2.2. The total urban and rural population for each province was extracted in ArcGIS 10.2.2 respectively for calculating the urban and rural population connectivity to WWTPs.

Future water use projection

Domestic and industrial per capita water use was estimated for 2030 to predict the WWTPs connectivity. Jia et al.[20] found that the industrial and domestic water use increased annually by 2% and 3% respectively from 2000 to 2011. The daily per capita water use in Chinese statistic year book[11] was relatively stable from 2008 to 2013 (Table S2-S3). Average of annual changing rates of domestic and industrial daily water use during 2008-2013 for each province was calculated and assumed to be the constant annual increasing rate from year 2013 to 2030. If the average is positive, upper limits of the annual increasing rates were assumed to be 2% and 3% respectively for industrial and domestic daily per capita water use; otherwise, the daily water use for 2030 was assumed to be the same with the average of annually daily water use during 2008-2013 for both domestic and industrial use in specific provinces, because it was unlikely that the per capita daily water use will decrease greatly with the progress of urbanization, economics and life quality.

Future infrastructure development and WWTPs connectivity

The infrastructure change related to the emission of the six chemicals was mainly the construction of new WWTPs, which would increase the sewage treatment capacity and

potentially reduce the chemicals released to the environment directly with the sewage. Therefore, the daily sewage treatment volume (STV) was estimated for year 2030 at the provincial level. The annual increasing rates of daily STV at provincial level were calculated for years 2004-2013[21] and an average was taken to be the annual increasing rate after year 2013 to predict the daily STV for 2030 based on year 2013. The national daily STV during 1961-2013 was shown in Figure S2, which increased rapidly during years 2005-2009 and the increase decelerated from year 2010. This was a general phenomenon almost for all provinces in China. Therefore the projection for 2030 based on annual data during 2004-2013 (historical ten years) would be relatively radical compared to a projection if only based on annual data during 2009-2013 (historical five years).

The selected organics would be mainly released with domestic sewage, however, the method for predicting the daily STV in this section accounted for total sewage from both industrial and domestic release. Agricultural water use was not considered to go through WWTPs and be related to emission of the six chemicals. To differentiate the domestic STV from the total STV, it was assumed that the ratio of daily domestic and industrial water use would be equivalent to the ratio of daily domestic and industrial STV via WWTPs for individual province, so the domestic sewage treated in WWTPs for 2030 could be calculated. If the estimated volume of domestic sewage treated via WWTPs was greater than the estimated volume of domestic water use in the same province in 2030, it would be corrected to be equal to the estimated domestic water use.

Domestic STV via WWTPs was divided by the domestic per capita water use for estimating the population which would be connected to WWTPs. Urban population was assumed to be assigned to the WWTPs first before any rural population for estimating respectively urban and rural population connectivity to WWTPs. The 'Urban drainage and sewage treatment bulletin of China (2006-2010)'[12] provided the annual volume of sewage released and treated in urban area at provincial level from 2006 to 2010 and the target of sewage treatment rates for the 12th five-year plan (2010-2015). The average national sewage treatment rate for urban area was ca. 79% for 2010. For a conservative estimation, if the urban population connectivity to WWTPs estimated by above method was less than 79% for a province, 79% would be assigned to this province.

Future emission inventory

Usage Mintel Global New Products database[16] provided the fraction of variants containing the individual chemical for each of 29 subcategories. All the six chemicals were assumed not to be banned or replaced by another chemical in products till 2030 in the Chinese market and formula were presumed to be constant between 2012 and 2030. Therefore, inclusion levels of

chemicals in subcategories were the same in 2030 with those shown in a previous study for 2012.[4] Combining above information and the Chinese market size in 2030, the total usage of chemicals in Chinese market for 2030 was estimated. It was allocated to counties across China by population projected for 2030.

Emissions Products estimated to be sold in 2030 in Chinese market were assumed to be used and released within the same year. The WWTPs removal ratio of each chemical in 2030 was assumed to be identical to that of 2012 stated in a previous study.[4] The emission of each chemical in 2030 was estimated combining the spatially distributed usage, WWTPs removal ratios and WWTPs connectivity for urban and rural population by county. The emissions by county were then allocated to the 50×50 km^2 grid by population using ArcGIS 10.2.2.

Comparison of two scenarios in 2012 and 2030

Paired sample T-Test was used to investigate if significant difference exists between the emission and environmental concentration of individual chemical for the two years across China in 50×50 km^2 grid cells. The estimated emissions and environmental concentrations (50×50 km^2) of chemicals for 2012 and 2030 were log-transformed for this statistic analysis.

Results and discussion

Infrastructure development and WWTPs connectivity The predicted daily per capita water use for 2030 ranges (mean) 73-371 (184) L/day/capita for domestic use and 73-1018 (328) L/day/capita for industrial use at provincial level (Table S2-S3). The highest daily per capita water use is in Fujian for domestic water use and Shanghai for industrial water use. Based on infrastructure construction progress rates during 2004-2013, 22 out of 31 provinces are predicted to have sewage treatment capacity greater than the predicted total domestic water use in 2030. After correction, the domestic sewage treated ranges 41-2753 with a mean of 924 (10,000 m^3/day) at provincial level (Table S4). Also the same 22 provinces have 100% sewage connected to WWTPs for both rural and urban population; and the other 9 provinces have the connectivity of 79-82% for urban population and 0 for rural population (Table S5).

This result is only developed on assumptions in one scenario. The development of infrastructure has decelerated since 2010 (Figure S2), so it is possible that the speed of construction of WWTPs after 2013 till 2030 will be slower than the average speed during the historical ten years (2004-2013) which is assumed in this study. However, in the 12th five-year plan, the target till 2015 is that the sewage treatment rates should be 100% for 36 municipalities, capital cities and other cities specifically designated in the state plan, above 70% for other cities or towns in China and above 30% for designated towns (lowest administrative level town).[12] It is reasonable to achieve that most cities or urban population are 100% connected to WWTPs after 15 years in 2030.

Market size and emission inventories

The increase of the market size of the 12 categories containing the six chemicals in 2030 compared to 2012 can be found in Table 1. The market size of hard surface care product is predicted to grow least and that of diapers & feminine hygiene is the greatest. The markets size of all subcategories (listed in Table S1) grows to the extent of 13-363% except for bar soap, of which the market size decreases by 28%. The average growth of the market size of all 29 subcategories is 124%. The market size of automatic dishwashing, conditioners & softeners and sun protection products is predicted to be over doubled from 2012 to 2030; and another 16 subcategories have the growth of sales over 100% from 2012 to 2030. With the development of economics and income during 2012-2030, Chinese consumers probably tend to have higher expenditure on these consumer products to improve their life quality and self-protection. This is the main reason of the general growth of the market size. Also more wealthy consumers will change their preference on products, e.g. they probably tend to use more liquid detergents and liquid soap rather than bar soap and begin to use automatic dishwashing. This leads to the diverse changing patterns of the market size of different subcategories over time.

Table 1 Predicted market size of different categories in 2030 and comparison with that in 2012

Categories	Market size in 2030 (Tonnes)	Market size in 2012 (Tonnes)	Change percentage
Oral Hygiene	570457	270867	111%
Soap & Bath Products	750451	584519	28%
Dishwashing Products	1676879	814400	106%
Fabric Care	7822828	4259900	84%
Skincare	261753	115029	128%
Hair Products	1259534	655501	92%
Diapers & Feminine Hygiene	32554	11815	176%
Deodorants	3848	1654	133%
Hard Surface Care	69604	57300	21%
Toilet Care	127023	45700	178%
Fragrances	1336	628	113%
Shaving & Depilatories	1631	772	111%

Also due to this, the composition of sources of the six chemicals slightly changes between the two years (Figure 1). Generally, except for climbazole, proportion of chemicals from soap & bath products (mainly bar soap) reduces for all other five chemicals, as climbazole is mainly used in hair products; and proportion of chemicals from hair products reduces for BP-3, OMC and OC. The proportion of chemicals from oral hygiene and skincare products increases due to a higher increasing rate of market size for the two categories of products than that for hair

products. Generally the main sources of the six chemicals will not change in 2030 compared to that in 2012.

There is possibly uncertainty in the projection of per capita GDP of China by OECD, which will lead to bias of market size projection. Research and development of the new subcategory of products may change the preference of consumptions and therefore the composition of chemical sources, which is unpredictable and will cause probably different results with the current projection for 2030. The possible change of formula and restriction of chemical use in the future in China may lead to varied results as well.

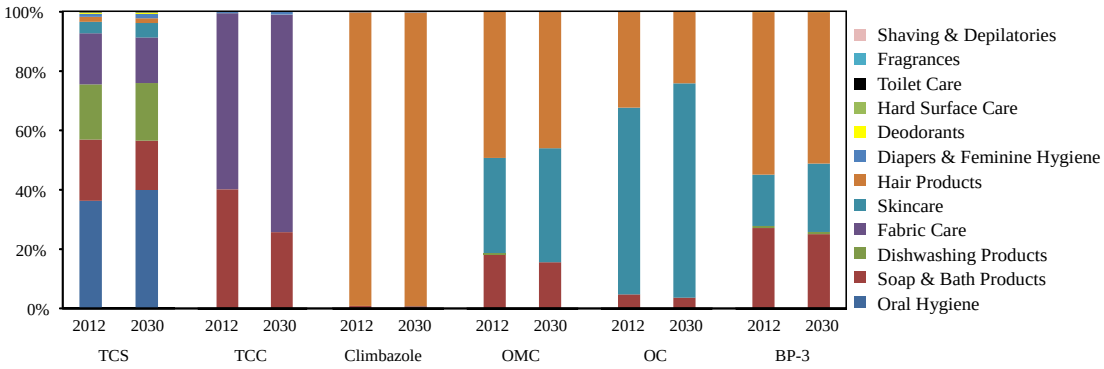

Figure 1 Composition of sources of the six chemicals from Chinese market in 2012 and 2030

Table 2 Usage, emission calculated by population allocation methods and the percentage of change from usage to emission of six chemicals for year 2012 and 2030

	2012			2030		
Abbreviation	Usage (tonnes)	Emission (tonnes)	Percentage change	Usage (tonnes)	Emission (tonnes)	Percentage change
TCS	179	111	-38%	342	52	-85%
TCC	74	47	-37%	97	14	-86%
Climbazole	135	110	-18%	253	161	-37%
BP-3	602	473	-21%	1264	706	-44%
OC	206	131	-36%	538	101	-81%
OMC	1080	692	-36%	2260	462	-80%

The predicted usage and emission of chemicals in Chinese market for both 2012 and 2030 is shown in Table 2. Emissions are estimated by usage population allocation method for both years for comparison. The usage of chemicals in 2030 is predicted to be about twice of that in 2012 except for TCC, although the usage of TCC also increases; in contrast, emissions in 2030 are not predicted to increase in the same rate due to the construction of WWTPs and therefore the chemical removal, e.g. by the paired sample T-test on the two emission groups in 2012 and 2030, in 2030 emissions decrease for TCS, TCC and OC; significantly increase for climbazole and BP-3; and do not have significantly change for OMC. The percentage of

chemical removed from usage to emission is about doubled from 2012 to 2030 for all chemicals.

Spatial distribution of the usage and emission Figure 2 shows the spatial distribution of TCS usage and emission by county for 2030 (those for the other five chemicals are in Figure S3-S4). Generally the chemical usage mostly distribute to the southeast of Hu Line, which is an imaginary straight line linking Heihe in Heilongjiang province and Tengchong in Yunnan province and reflects the significant difference of population on the two sides of Hu Line. The spatial pattern of chemical usage aligns that of population due to the allocation method used in this study (Figure S5).

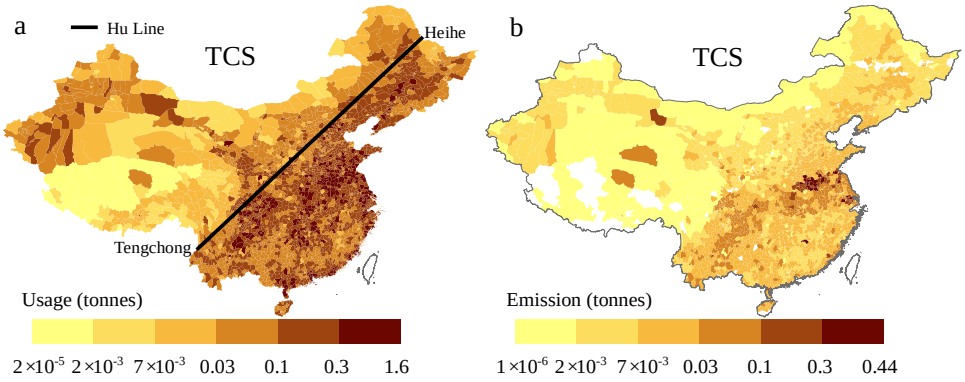

Figure 2 The spatial distribution of TCS usage (a) and emission (b) by county across China in 2030 and the Hu Line (Heihe-Tengchong Line)

The spatial pattern of emission (Figure 2b) is significantly different with that of usage or population due to the chemical removal via WWTPs. Highest emissions are predicted to mainly distribute in north Anhui, southeast Henan, north and south of Jiangsu and northwest of Gansu. These regions have high chemical usage but lower sewage connectivity to WWTPs. Some other regions such as Hubei, Chongqing and west Guizhou also have higher emissions than the other areas due to the high usage. After allocating the emission to fit the model resolution of 50×50 km^2, the range (5^{th} - 95^{th}, median) of emission (tonnes) across China are 4×10^{-5}-0.09 (median, 0.005) TCS, 9×10^{-6}-0.02 (0.001) TCC, 3×10^{-4}-0.25 (0.03) climbazole, 1.5×10^{-3}-1.1 (0.12) BP-3, 1.2×10^{-4}-0.15 (0.01) OC and 6×10^{-4}-0.69 (0.06) OMC. The median emission is approximately equal to that in 2012 for climbazole and BP-3; about only half of that in 2012 for TCS, OC and OMC; and only 1/10 of that in 2012 for TCC.

Environmental concentrations The range of environmental concentrations (5^{th} - 95^{th}, plus mean) in China in 2030 are predicted as follows: for freshwater, 6.7×10^{-4}-16 (mean, 4) ng/L for TCS, 4×10^{-4}-10 (2.4) ng/L for TCC, 0.14-331 (81) ng/L for climbazole, 0.4-1241 (302) ng/L for BP-3, 9.5×10^{-4}-41 (10) ng/L for OC and 0.01-263 (62) ng/L for OMC ; for sediment, 2.4×10^{-4}-6 (1.3) ng/g for TCS, 1.4×10^{-3}-31 (8) ng/g for TCC, 4.8×10^{-3}-13 (3) ng/g for

climbazole, 0.02-60 (15) ng/g for BP-3, 4.3×10^{-3}-143 (33) ng/g for OC and 0.01-159 (37) ng/g for OMC. Compared to the year 2012, in 2030 the national mean concentration is approximately equivalent to that in 2012 for BP-3 and OMC in freshwater but reduces for the other four chemicals; the 5^{th} percentile concentration in freshwater is predicted to be higher than that in 2012 except for TCC; and the 95^{th} percentile concentration in freshwater is predicted to be lower than that in 2012 except for BP-3 and climbazole, which is predicted to be approximately constant to that in 2012. The same rules can be concluded for estimated concentrations in sediment.

Generally, the higher concentration in aquatic system is predicted to distribute in west Guizhou and boundary of Henan and Anhui provinces rather than the other regions for almost all chemicals (Figure S6-S7). This aligns the spatial pattern of emissions. BP-3 and climbazole also have higher concentration in certain regions in west Xinjiang, Liaoning and North China Plain (NCP) than the other regions. This is different with conclusions for 2012 in our previous study,[4] in which NCP and coastal regions in Jiangsu, Zhejiang, Fujian and Guangdong have higher concentration than other regions.

Table 2 indicates the significant contribution of WWTPs construction to chemical removal before entering the Chinese environment. Despites the more removal, not all chemicals have significantly decreased emissions in 2030 compared to that in 2012 as discussed above. However, concentrations in aquatic system of all six chemicals are predicted to be significantly lower in 2030 than that in 2012. This indicates the greater future river discharge flow in 2030 than that in 2012 dilutes the chemical contents in aquatic system after released.

Key factor and implication on future research and applications In this study, the future expansion of consumer products consumption in 2030 does not increase the environmental concentration of the selected six organic chemicals ultimately in China due to two main reasons, i.e. rapid WWTPs construction across China and dilution of higher river discharge flow. WWTPs construction is believed to be the more important factor among the two and more realistic to be controlled. The projected river discharge flow in 2030 is only based on one climate change scenario, which is also a natural factor that is highly uncertain. Therefore it is important to improve the infrastructure in China especially in regions with high population.

Only one scenario is considered in this study. Assumptions on continual use of these chemicals as ingredients without being banned or replaced in formula and constant removal ratio of chemicals in WWTPs without technical improvement will probably lead to overestimation of emissions and environmental concentrations; and assumptions on rates of infrastructure construction based on historical ten years will probably cause underestimation

of emission and environmental concentrations. Different scenarios can be projected and compared in the future study to include the different possibilities. For example, (1) a more conservative rate for the infrastructure construction; (2) technical improvement of sewage treatment, i.e. a higher removal ratio in WWTPs or (3) relevant policy change which may affect the result of estimations, e.g. the population projection in this study for 2030 has not considered different population policy; however, one-child policy may end in the near future based on the announcement from a recent state conference,[22] which will probably bring more population.

Such future scenario studies and model application can be also applied on many other chemicals such as pharmaceuticals, which are more similar to the six selected organic chemicals in this study on emission pathway than other chemicals but more active and toxic. The challenge for this group of chemicals is the estimation of emission distribution of veterinary use, which will require the information on animal population and distribution (e.g. pig and chicken etc.) for a more accurate projection. Higher connectivity to WWTPs in rural area for especially the release from veterinary use and the future river dilution will probably reduce the emission and concentration in aquatic system. The results of such study can probably provide reference for research need, business strategy with consideration of environmental sustainability and government plan on the infrastructure construction.

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Supporting Information for

Projected changes in environmental conditions, population, infrastructure and consumer spending on the use, emission and environmental distribution of selected organic chemicals in China

Ying Zhu[1], Oliver R. Price[2], John Kilgallon[2], Yi Qi[3], Shu Tao[4], Kevin C. Jones[1], and Andrew J. Sweetman[1*]

[1]Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, United Kingdom

[2]Safety and Environmental Assurance Centre, Unilever, Sharnbrook MK44 1LQ, United Kingdom

[3]Department of Urban Planning & Design, Nanjing University, Nanjing 210093, China

[4]Laboratory for Earth Surface Processes, College of Urban and Environmental Sciences, Peking University, Beijing 100871, China

*Corresponding author email:

Andrew J. Sweetman, a.sweetman@lancaster.ac.uk

13 pages; 8 figures; 5 tables

S1. Regression of per capita GDP and market size of different categories of products during 2000-2019 in China

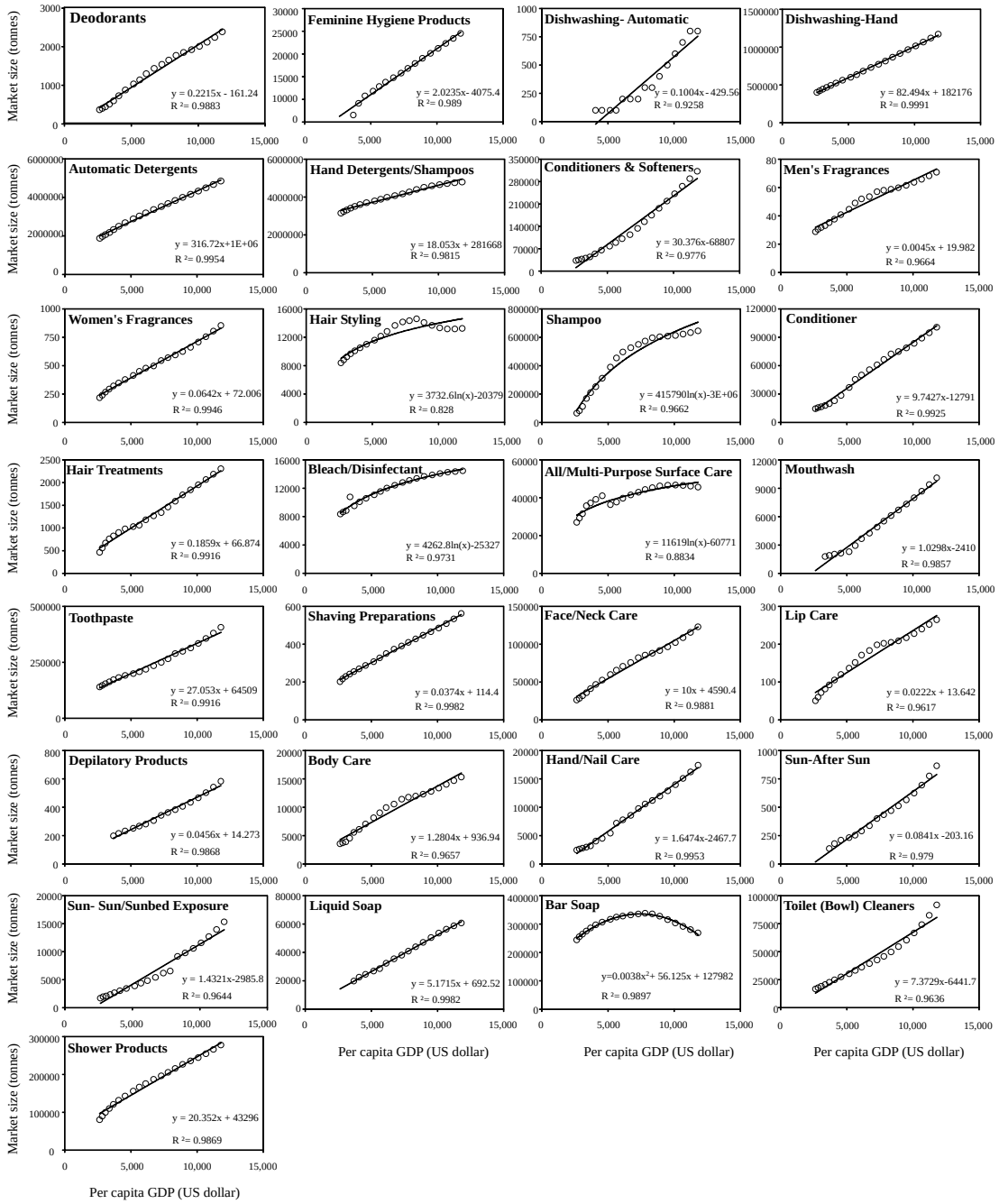

Figure S1 Regression of per capita GDP and market size of consumer products in China during 2000-2019

Table S1 Categories and subcategories of products containing selected chemicals

Categories	**Subcategories**
Oral Hygiene	Mouthwash
	Toothpaste
Soap & Bath Products	Bar Soap
	Liquid Soap
	Shower Products
Dishwashing Products	Dishwashing - Automatic
	Dishwashing - Hand
Fabric Care	Automatic Detergents
	Conditioners & Softeners
	Hand Detergents/Shampoos
Skincare	Body Care
	Face/Neck Care
	Hand/Nail Care
	Lip Care
	Sun - After Sun
	Sun - Sun/Sunbed Exposure
Hair Products	Conditioner
	Hair Styling
	Hair Treatments
	Shampoo
Diapers & Feminine Hygiene	Feminine Hygiene Products
Deodorants	Deodorants
Hard Surface Care	All-Purpose/Multi-Purpose Surface Care
	Bleach/Disinfectant
Toilet Care	Toilet (Bowl) Cleaners
Fragrances	Men's Fragrances
	Women's Fragrances
Shaving & Depilatories	Depilatory Products
	Shaving Preparations

S2. Infrastructure and water use

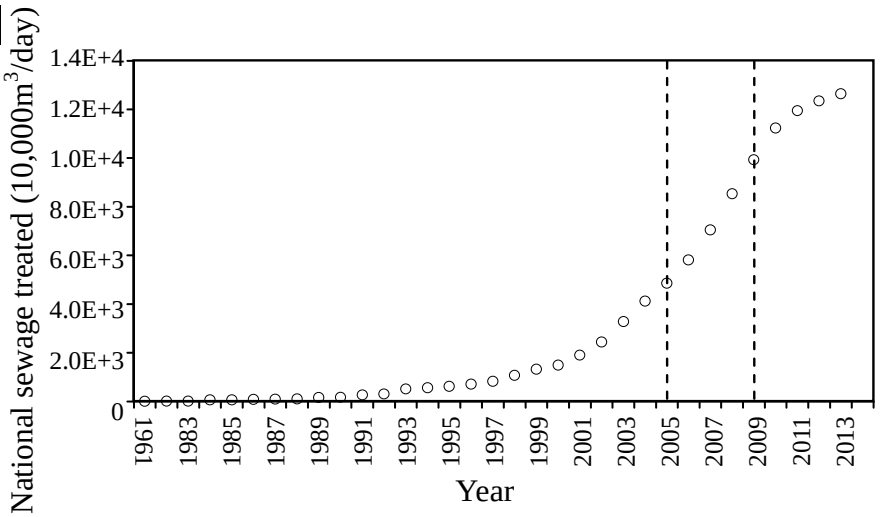

Figure S2 the national sewage treated (10,000 m^3/day) in China from 1961 to 2013

Table S2 Provincial domestic water use during 2008-2013 and the projection for 2030 (L/capita/day)[1]

Provinces	2008	2009	2010	2011	2012	2013	2030
Anhui	123	130	139	139	141	143	236
Beijing	252	239	214	208	212	211	223
Chongqing	169	175	177	175	163	167	171
Fujian	167	167	168	167	208	224	371
Gansu	96	112	115	115	98	84	103
Guangdong	259	257	247	246	247	244	250
Guangxi	286	273	276	274	214	222	258
Guizhou	117	107	130	130	103	126	199
Hainan	202	204	206	204	204	210	238
Hebei	92	91	91	91	88	89	90
Heilongjiang	135	135	126	126	117	122	127
Henan	102	103	105	105	93	97	101
Hubei	148	148	155	154	147	186	307
Hunan	194	197	194	193	166	164	185
Inner Mongolia	167	159	166	166	114	118	148
Jiangsu	177	182	184	184	175	177	180
Jiangxi	146	161	169	168	159	163	241
Jilin	133	141	163	163	119	122	140
Liaoning	156	155	160	159	146	146	154
Ningxia	73	76	77	76	68	68	73
Qinghai	165	165	171	169	104	108	147
Shaanxi	102	108	109	109	108	110	143
Shandong	99	101	104	103	93	94	99
Shanghai	327	329	279	274	286	292	298
Shanxi	79	80	81	81	90	92	153
Sichuan	116	121	129	129	145	136	224
Tianjin	117	114	116	111	97	94	108
Tibet	218	192	183	181	92	90	159
Xinjiang	158	190	160	158	147	142	159
Yunnan	135	141	136	135	113	120	130
Zhejiang	195	199	198	198	208	212	280

Table S3 Provincial industrial water use during 2008-2013 and the projection for 2030 (L/capita/day)[1]

Provinces	2008	2009	2010	2011	2012	2013	2030
Anhui	381	419	432	432	454	447	626
Beijing	84	81	71	69	65	66	73
Chongqing	444	456	450	445	367	373	422
Fujian	573	583	603	598	554	544	576
Gansu	136	136	147	147	167	139	162
Guangdong	394	387	364	362	314	308	355
Guangxi	294	304	328	326	301	333	527
Guizhou	244	246	270	271	312	211	259
Hainan	157	124	121	120	118	117	126
Hebei	99	92	88	87	95	94	93
Heilongjiang	412	399	400	400	298	243	359
Henan	149	155	162	162	176	173	242
Hubei	465	483	560	557	577	437	513
Hunan	352	357	374	373	405	386	538
Inner Mongolia	232	237	250	249	259	259	379
Jiangsu	747	690	668	665	668	759	836
Jiangxi	373	329	352	350	357	364	354
Jilin	193	236	261	260	270	264	369
Liaoning	157	152	156	156	143	143	151
Ningxia	148	161	178	177	206	210	294
Qinghai	388	147	159	157	121	139	185
Shaanxi	94	83	88	88	97	100	132
Shandong	72	71	77	76	79	81	124
Shanghai	1154	1200	1010	990	839	912	1018
Shanxi	108	84	96	96	118	112	157
Sichuan	194	206	214	214	186	197	216
Tianjin	89	97	102	98	99	100	152
Tibet	126	130	134	133	147	146	204
Xinjiang	126	128	140	139	152	155	217
Yunnan	133	134	152	151	164	148	220
Zhejiang	327	293	300	299	304	293	303

Table S4 predicted total and domestic sewage to be treated for 2030

Provinces	Ratio (domestic water use to total water use)	Total sewage treated (10,000 m^3/day)	Domestic sewage treated (10,000 m^3/day)	Corrected domestic sewage treated (10,000 m^3/day)
Anhui	27%	6240	1709	1709
Beijing	75%	1009	761	475
Chongqing	29%	13431	3869	906
Fujian	39%	1453	569	569
Gansu	39%	1234	482	356
Guangdong	41%	15413	6370	2753
Guangxi	33%	5225	1716	1677
Guizhou	43%	41148	17885	1084
Hainan	65%	306	200	200
Hebei	49%	10630	5249	919
Heilongjiang	26%	7268	1896	840
Henan	29%	8686	2557	1612
Hubei	37%	27019	10120	2231
Hunan	26%	2679	685	685
Inner Mongolia	28%	1520	427	427
Jiangsu	18%	6225	1103	1103
Jiangxi	41%	5163	2093	1610
Jilin	28%	745016	204988	437
Liaoning	50%	3728	1879	813
Ningxia	20%	203	41	41
Qinghai	44%	1073	475	98
Shaanxi	52%	5448	2835	738
Shandong	44%	10527	4664	1188
Shanghai	23%	3244	734	613
Shanxi	49%	6192	3059	1091
Sichuan	51%	3679	1874	1874
Tianjin	41%	817	339	153
Tibet	44%	0	0	0
Xinjiang	42%	1101	466	412
Yunnan	37%	1130	420	420
Zhejiang	48%	3706	1782	1619

Table S5 Provincial urban/rural population and connectivity to WWTPs

Provinces	Population	Urban population	Rural population	Population connected	Urban connectivity	Rural connectivity
Anhui	117119298	88154633	28964665	72355253	82%	0%
Beijing	21326111	21002993	323119	34181530	100%	100%
Chongqing	52988167	52659358	328808	226383191	100%	100%
Fujian	40793437	38620606	2172831	15340047	79%	0%
Gansu	34363991	33001848	1362143	46545047	100%	100%
Guangdong	110151883	98365560	11786323	254863304	100%	100%
Guangxi	65068997	64419905	649092	66593773	100%	100%
Guizhou	54422168	53898010	524159	897755655	100%	100%
Hainan	10454493	10247246	207247	8407138	82%	0%
Hebei	101785559	66405781	35379777	581266867	100%	100%
Heilongjiang	66299925	51983952	14315972	149729812	100%	100%
Henan	159463149	112824824	46638325	252993223	100%	100%
Hubei	72617478	70265693	2351785	329326649	100%	100%
Hunan	92329040	90695254	1633786	37088761	79%	0%
Inner Mongolia	28780830	4723300	24057530	28804420	100%	100%
Jiangsu	116267512	85010145	31257367	61292116	79%	0%
Jiangxi	66678283	63864745	2813538	86671809	100%	100%
Jilin	31136411	12418046	18718365	14620388738	100%	100%
Liaoning	52918440	17381773	35536667	122321206	100%	100%
Ningxia	23101339	21682929	1418410	5544220	79%	0%
Qinghai	6680962	6041756	639206	32323219	100%	100%
Shaanxi	51525077	44709047	6816030	198053860	100%	100%
Shandong	120143165	78177300	41965865	471733229	100%	100%
Shanghai	20574898	20284960	289938	24657532	100%	100%
Shanxi	71388875	67774614	3614261	200162747	100%	100%
Sichuan	132320253	128799655	3520598	83617887	79%	0%
Tianjin	14144119	13981714	162405	31401617	100%	100%
Tibet	4052703	3878951	173752	0	79%	0%
Xinjiang	25874569	9299455	16575114	29293608	100%	100%
Yunnan	57155999	55184206	1971793	32341897	79%	0%
Zhejiang	57754968	47969517	9785451	63573020	100%	100%

S3. Usage and emission by county

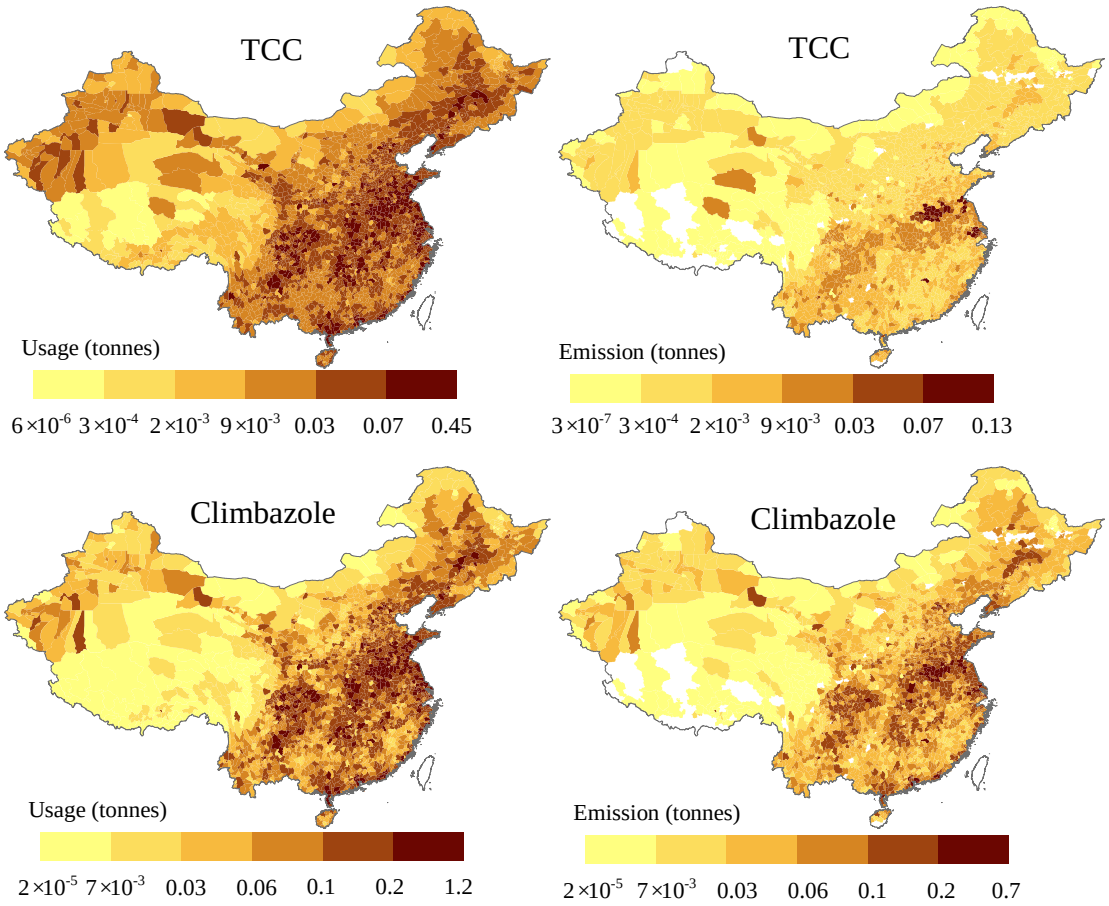

Figure S3 Usage and emissions of antibacterial agents by county in China in 2030

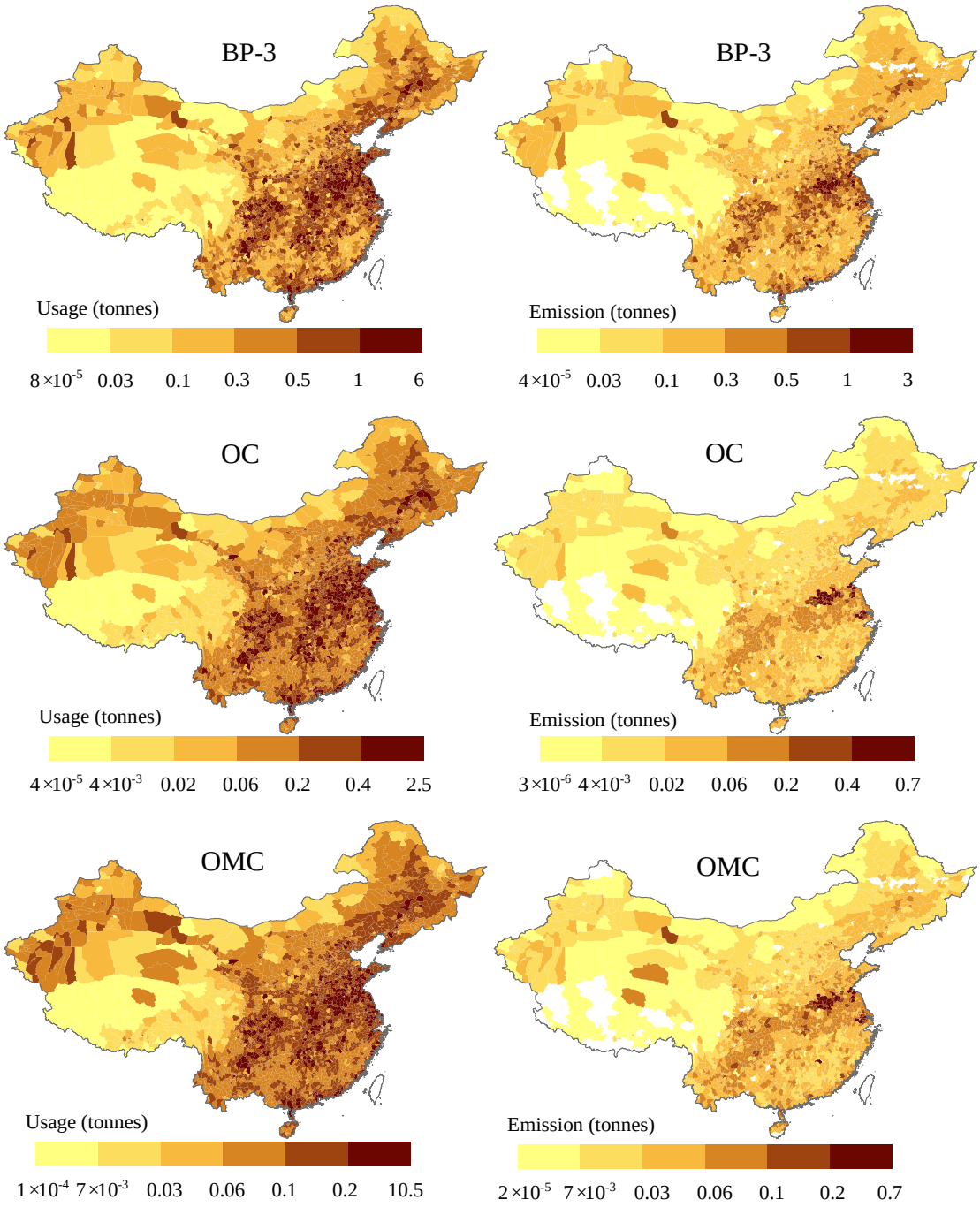

Figure S4 Usage and emissions of three UV filters by county in China in 2030

S4. Population

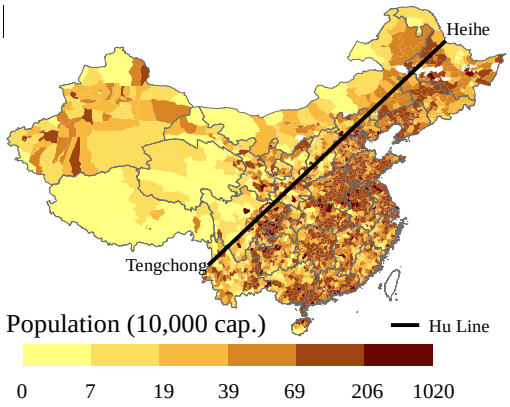

Figure S5 Population and spatial distribution by county in China for 2030[2] and Hu Line (Heihe-Tengchong line)

S5. Environmental concentration

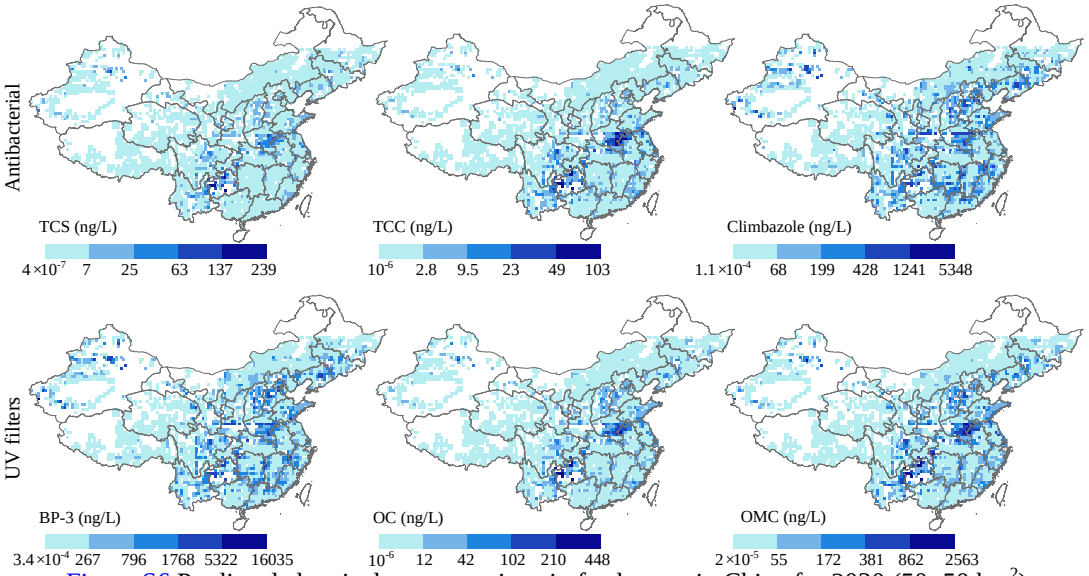

Figure S6 Predicted chemical concentrations in freshwater in China for 2030 (50×50 km^2)

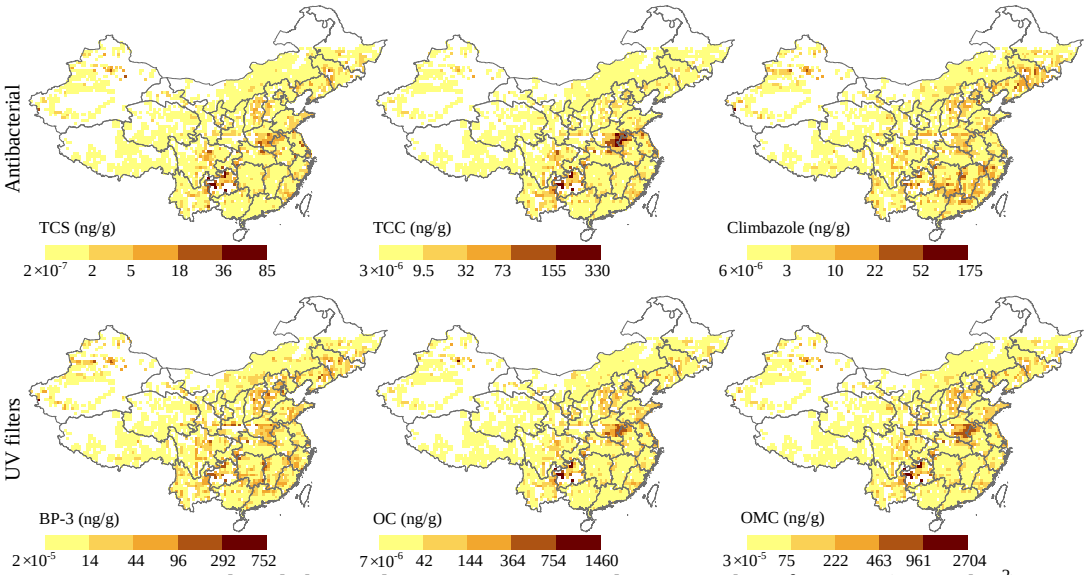

Figure S7 Predicted chemical concentrations in sediment in China for 2030 (50×50 km^2)

S6. River flow

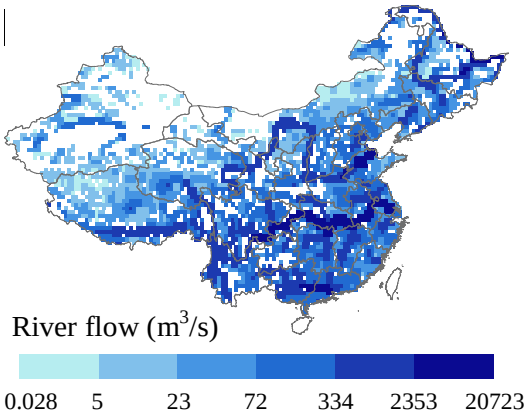

Figure S8 Predicted river flow rates in China for 2030[3] (50 ×50 km^2)

Reference:

(1) China Statistical Yearbook. http://www.stats.gov.cn/tjsj/ndsj/

(2) Han, J.; Feng, Y.; Qi, Y. Projection of development scale, spatial arrangement and development quality of Chinese cities in 2030 (*In Chinese, in preparation*). 2015.

(3) WATCH Driving Data 21st Century. http://www.eu-watch.org/data_availability